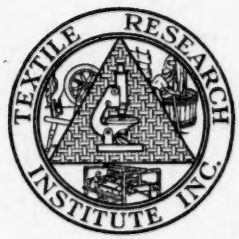
TEXTILE RESEARCH JOURNAL

VOLUME XIX October, 1949 *NUMBER 10*



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Manuscripts and communications should be sent to the editorial offices, 10 East 40th Street, New York 16, N. Y.

Subscription rates: General—$15.00 per year; additional for postage, 50 cents to Canada, $1.00 to all other countries. Special—$10.00 per year for United States and Canadian students, teachers, educational institutions, public libraries, governmental libraries and departments, plus 50 cents for postage to Canada. Single copies, $1.50 each.

Entered as second-class matter, April 27, 1945, at the postoffice at Lancaster, Pa., under the Act of August 24, 1912.

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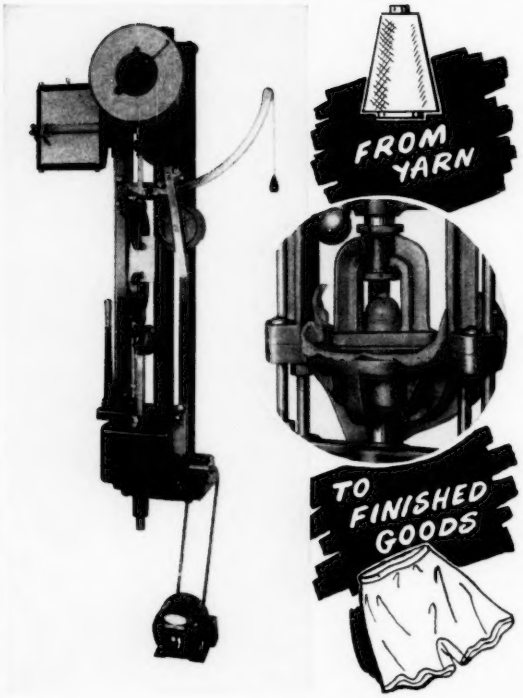

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TEXTILE RESEARCH JOURNAL

VOL. XIX, NO. 10 OCTOBER, 1949

The Fine Structure of Cotton Fibers from Density Measurements*

Helmut Wakeham†

Institute of Textile Technology, Charlottesville, Virginia

Abstract

Research on the apparent densities of cellulose fibers in different liquids gives information concerning inner fiber structure which may be useful in characterizing certain desirable properties of cotton fibers. The following report describes an investigation of some factors involved in evaluating density data in terms of fiber structure. The interpretation is made of some experimentally determined densities of cotton and rayon fibers in benzene and in dioctyl phthalate —two liquids differing greatly in molecular dimensions—and in mercury, a nonwetting liquid. In the last case, the "over-all density" of a fiber, defined as the average density of all material within the outer wall of the fiber, is determined by a method utilizing a mercury-pressure volumenometer.

In the case of the wetting liquids, higher densities were obtained with benzene—which has the smaller molecule; this indicates that the fibers have pore spaces which in size approach the dimensions of the molecule. When the cotton fibers are cut into short sections, about 1 mm. long, more of these pores and intrafiber channels are open to the liquid medium; a higher density is, therefore, obtained for the cut fibers than for the whole fibers. Pore-space values within the fiber are calculated and compared with values obtained by other methods. The significance of these observations in the consideration of fiber structure is discussed.

DETERMINATION OF THE DENSITY, or mass per unit volume, of a substance requires evaluation of the weight and the volume of a given sample of the material. The weight of a sample of textile material is relatively easily measured, but the determination of volume presents a rather difficult problem. Fortunately, the very difficulties encountered in volume measurement are due to the peculiarities of fiber structure which the investigator in the field is anxious to discover. A careful study of textile fiber density should lead, theoretically at least, to useful information concerning the inner structure of the textile fiber.

There is considerable evidence indicating that cellulose fibers contain pores, the dimensions of which are far larger than the dimensions of most molecules [1, 3, 14, 16]. Some fibers, such as cotton, have a lumen, and the existence of much finer microscopic or even submicroscopic capillary spaces seems alto-

* This work was reported in part at the Spring, 1948, meeting of the Fiber Society, Fontana Village, North Carolina.

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TABLE I. DENSITIES OF AMERICAN UPLAND COTTONS AND VISCOSE RAYONS IN VARIOUS MEDIA AS REPORTED IN THE LITERATURE

Medium	Cotton	Rayon	Author
Helium	1.567	1.548	Davidson [6]
Toluene	1.550	1.543	Davidson [6]
Benzene	1.546	1.513	Bredee [5]
Heptane	1.540	1.516	Blitz [4]
Carbon tetrachloride	1.534	1.524	Moll [19]
Water	1.610	1.608	Davidson [6]
Calculated crystalline density	1.593	1.591	*

* Calculated by the author, using the lattice dimensions of Meyer and coworkers [17, 18, 26].

gether possible. When such fibers are immersed in a wetting but nonswelling liquid by some method which excludes traces of moisture and air, the fiber pores are filled with the liquid to an extent depending upon the size of the liquid molecules and upon the accessibility of the space to the outer atmosphere by means of suitable channels for entrance. Certain rayons, for example, are known to contain submicroscopic bubbles formed during the coagulation of the fiber [13]. These bubble spaces are completely surrounded by compact cellulose; they may not be filled by the liquid unless a swelling agent is used.

The volume of an irregular object—such as a textile fiber—is usually measured by a displacement method. The volume of the fluid displaced (and the apparent fiber volume) will be greater when the fluid fails to penetrate some of the empty spaces of the fiber. Consequently, the observed density is lower than that obtained when the fluid completely fills all the empty spaces within the fiber.

The concept that there are empty spaces within the fiber must be carefully defined in interpreting fiber density data. It is well known that only part of the cellulose in the fiber is organized into a crystalline lattice; the remainder is noncrystalline cellulose in regions where the chains may be considerably farther apart than they are in the crystalline regions. The regions of greatest density are, therefore, those composed of crystalline cellulose; the noncrystalline cellulose will be contained in regions of lower density in which empty spaces will also occur. Some of these spaces will be large; others very small. Some will be open to the outer atmosphere by means of small capillaries; others will be completely closed off. Some will be filled by the fluid in which the fiber is immersed; others will remain empty.

If one could choose a nonswelling fluid which penetrates all the spaces in the fiber except those between the cellulose chains in the crystalline regions, he would obtain a density value corresponding to that of crystalline cellulose. Davidson [6] hoped to find such a fluid in helium, one of the smallest atoms known, but later determination of the crystalline density showed that both cotton and rayon have spaces which even helium will not penetrate. Densities obtained with benzene, toluene, heptane, carbon tetrachloride, or any other nonswelling liquid are all lower than that calculated for crystalline cellulose because some of the interchain spaces are not filled with the liquid upon immersion. (See Table I.) In fact, Hermans [9, 11] has attempted to evaluate the ratio of crystalline to noncrystalline cellulose in several fibers by assuming that the lower density is due only to interchain spaces in noncrystalline regions.

Attention is called to the fact that water is not a suitable medium for cellulose fiber density determination because it causes the fiber to swell and to lose its shape. Some of the water taken up by the fiber, moreover, is held so tightly by the cellulose that the observed density of the fiber is, in some cases, greater than that of crystalline cellulose [6, 7, 8, 23].

Although it should be possible, by the use of apparent density measurements with nonswelling wetting liquid immersion media, to obtain some information concerning the nature of pore spaces in the cotton fiber, the method cannot be used to study pores appreciably larger than the dimensions of the molecules of which the liquid is composed. This fact places a rather serious limitation on the usefulness of the method in studying fibers. It seems reasonable that the pore spaces in cotton, for example, exist in a wide range of sizes, from that of the lumen down to the interchain spaces of molecular dimensions. Any wetting liquid medium used will readily penetrate at least some of the larger pores and will prevent measurement of the minimum apparent density conceivable—the density of the fiber as a whole.

The fact that wetting liquids penetrate large fiber pores suggests the use of a nonwetting liquid as the immersion medium. Such a liquid would not spontaneously penetrate the pore spaces and would permit measurement of an "over-all" fiber density which could be used to evaluate the total free space in the fiber. The "over-all density" is here defined as the average density of all cellulose and free space within

the outer wall of the fiber, or as that enclosed, for example, by the perimeter of the fiber cross section. Such a density value might also be useful in connection with certain physical tests requiring such data.

Mercury is a nonwetting liquid which has been employed in a mercury-pressure volumenometer for studying the pore-space distribution in porous, rigid solids [22]. The relatively great flexibility and compressibility of cellulose fibers limits the use of a similar method with them. The method can, however, be used to obtain the over-all fiber density, and for this purpose it is utilized in the present investigation.

Experimental Procedures

Pycnometric Method

Apparent densities in benzene and dioctyl phthalate as wetting liquids were measured by the pycnometric method. Samples of the fiber, weighing about 1 g. each, were stuffed into 10-cc. calibrated pycnometer bottles and dried to constant weight by evacuation to about 0.01 mm. of mercury pressure at room temperature. The pycnometers were then placed in the filling tube sketched in Figure 1A. The benzene in the left arm of the tube was then frozen by surrounding the tube with a dry ice-acetone mixture to permit evacuation of the tube without losing the benzene. The tube was next cut off from the evacuation system by turning the stopcock. The benzene was then melted and frozen again to remove any dissolved air during the second evacuation. After the pressure in the tube was again reduced in this manner, the stopcock was closed and the tube was tilted through 90°, as shown in Figure 1B. Opening the stopcock in this position forced the benzene into the pycnometer and into the fiber contained therein. The pycnometer was then brought to constant temperature in a bath at 30.3°C and weighed. From the filled weight, the weight and volume of displaced benzene and the volume occupied by the fiber were calculated.

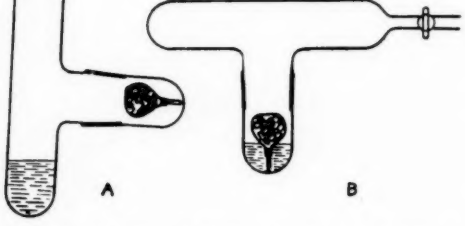

FIG. 1. *Diagram of filling tube used in density determination.* A—*Normal position of the tube during evacuation and degassing.* B—*Position during filling operation.*

Densities were also measured in dioctyl phthalate, a liquid composed of molecules about three times as large as the benzene molecule. The filling procedure was the same as that outlined above except that the freezing procedure was dispensed with, the vapor pressure of the liquid being less than 0.02 mm. at room temperature.

It was found that fibers cut into short segments gave higher densities than whole fibers. The cut fibers were obtained by passing the fibers through a laboratory Wiley mill. When the mill was fitted with a 20-mesh screen the fiber fragments averaged about a millimeter in length. The ratio of length to cross-sectional diameter was, hence, still fairly large. Figure 2 shows a longitudinal view of the cut fibers for two samples. The photographs show some fraying of the cut ends, but this damage is not believed to be a serious factor in density determinations because the damaged portion represents a very small fraction of the cut sections.

Mercury-Pressure Method

Theory.—The mercury-pressure method involves submerging the vacuum-dried fiber in mercury within a volumenometer [22]. This instrument is then placed in a pressurizing system in which the volume occupied by the mercury and the fiber can be determined as the pressure on the system is increased. The mercury gradually penetrates the *interfiber* spaces until each fiber is completely surrounded. The volume of the fiber material is then the total volume minus the volume of mercury present.

The theoretical basis for this density measurement lies in the fact that surface forces oppose the entrance of mercury into small capillaries. (This effect is the common phenomenon of capillary depression observed in nonwetting liquids.) The opposing forces may be overcome by the application of external pressure; and the pressure required to fill a given pore is a measure of the size of the pore [24, 25]. The equation relating pressure and pore radius is

$$pr = -2\sigma \cos \theta, \qquad (1)$$

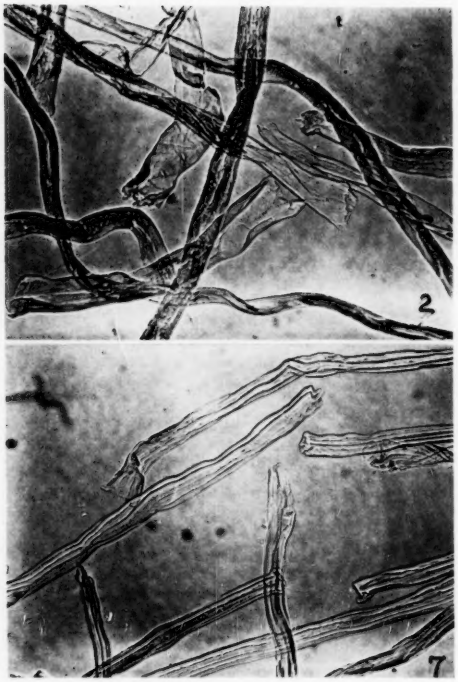

FIG. 2. *Photomicrographs of cut cotton and rayon fibers (Samples 2 and 7). (Magnification 200×.)*

where p is the absolute pressure, r the pore radius, σ the surface tension, and θ the contact angle. For mercury, we have used $\sigma = 475$ dynes/cm. at 25° C and $\theta = 180°$.

From this relation it appears that, at zero pressure, no nonwetting liquid will penetrate the porous mass upon immersion. When the pressure is raised to some finite value, the liquid will penetrate and fill all pores having radii larger than that calculated from equation (1).

When the mercury surrounds a mass of cotton fibers within an evacuated vessel, some of the larger interfiber spaces are filled because the column of mercury in the volumenometer exerts some pressure on the fiber system. Mercury is forced into additional spaces by releasing the vacuum. At an atmospheric pressure of 14.7 p.s.i.a. (pounds per square inch, absolute), it is calculated from equation (1) that the mercury will fill all interfiber spaces larger than 18 microns (0.018 mm.) in diameter. This diameter is about that of a mature cotton fiber. In order to obtain a correct density value for the whole fiber, the mercury must completely surround each individual fiber but must not penetrate the lumen or other spaces in the fiber. This extent of penetration of the fibrous mass is achieved by selecting a pressure of about 165 p.s.i.a., at which all spaces down to about 1.7 microns (0.0017 mm.) in diameter are filled with mercury.

Procedure.—The volumenometer used in these determinations consisted of an ordinary 10-cc. pycnometer bottle fitted with a calibrated capillary tube 20 cm. long. About 1 g. of fiber sample was stuffed into the bottle, dried, and surrounded with mercury by using the method described for the wetting liquids. The mercury-filled volumenometer was then weighed and placed in the pressurizing apparatus. This latter consisted of a heavy glass tube fitted with suitable safety housing and pressure connections (Figures 3 and 4). A cathetometer was used to measure the height of the mercury column in the capillary as the pressure was raised stepwise to 200 p.s.i.a. From these values, from the weights of mercury and dry fiber in the volumenometer, and from the calibrated volumes of the volumenometer and capillary, the apparent densities of the fiber were calculated at various pressures. (The compressibility of mercury and of the glass volumenometer were taken into account in these calculations.)

Typical density *vs.* pressure curves are shown in Figure 5. These curves show the expected leveling off of the density at high pressures. Here the interfiber spaces are all filled with mercury and the individual fibers are completely surrounded by the liquid. The density values at these high pressures (165 p.s.i.a.) have been taken as the true over-all densities of the fibers. In this manner the mercury values recorded in Table III have been obtained.

Fiber Samples and Results

Five raw cotton, one absorbent cotton, and one viscose rayon tow samples were studied in the preliminary investigation using the methods described above. The characteristics of these samples are summarized in Table II. The cotton samples varied considerably in staple length, fineness, and maturity, although a very coarse cotton was not included in the group. Figure 6 shows photomicrographs of cross sections of the immature and mature cottons (Samples 4 and 5).

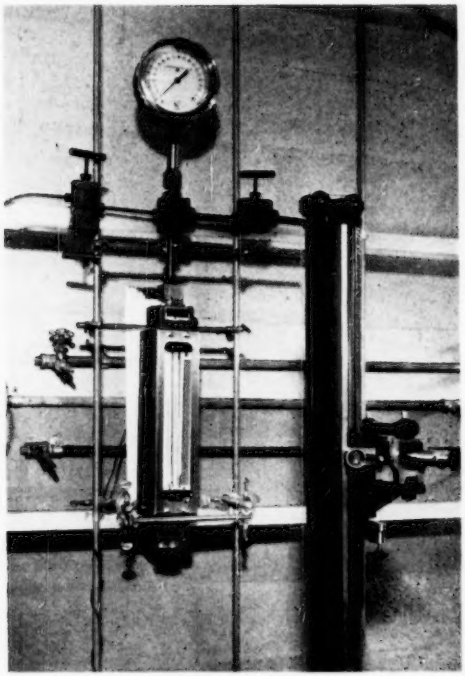

FIG. 3. *Apparatus used for determination of fiber density by the mercury-pressure method. Pressure vessel is on the left, cathetometer on the right.*

(For a survey of cotton fiber structure and properties, the reader is referred to the recent review by Berkley [2].)

The density values obtained in the manners described are shown in Table III. Each value in this table is the average of four determinations which agreed within 0.01 density unit of the average value. The densities reported are thus significant to a few parts in the third decimal place.

Discussion

Examination of the data in Table III reveals two general relationships: first, the densities of the cotton fibers in benzene are, for the most part, higher than the corresponding densities in dioctyl phthalate; second, the densities of the cut fibers are higher than those of the whole fibers. Both of these observations are highly significant in terms of the fiber-structure problem. They will be considered in detail in the following discussion.

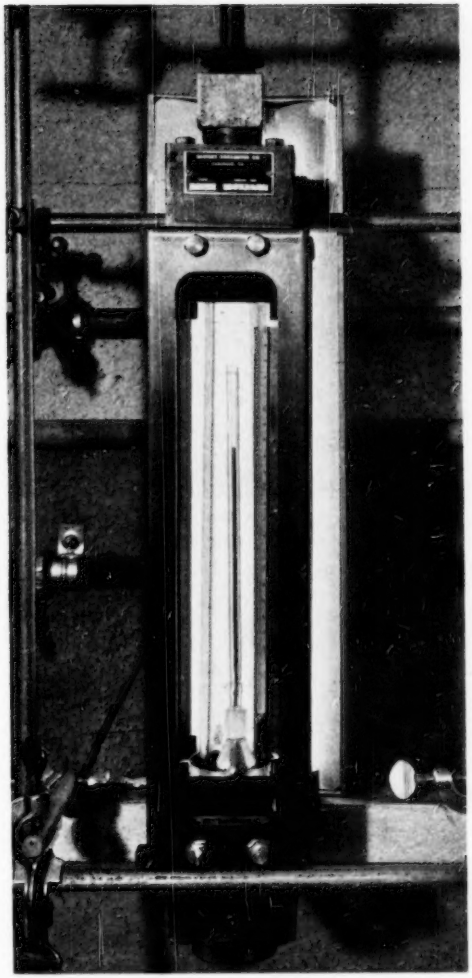

FIG. 4. *Close-up view of pressure vessel containing volumenometer. The mercury in the capillary tube can be clearly seen against the white background at the center of the vessel.*

Davidson [6] determined the apparent specific volume (reciprocal of apparent density) of a soda-boiled cotton sample in acetone, chloroform, benzene, carbon tetrachloride, nitrobenzene, and toluene. With these liquids he obtained values which differed from one another by less than the experimental error in the determination.

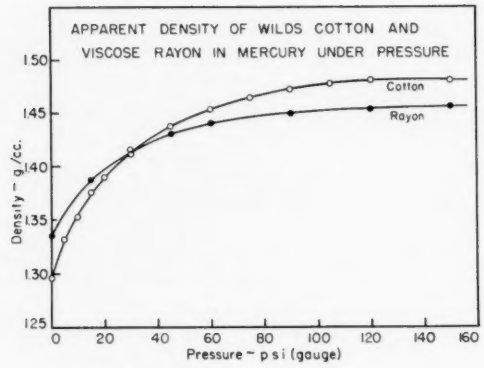

FIG. 5. *Typical curves of density vs. pressure.*

If it is true that cotton fibers contain pore spaces of molecular dimensions, it should be possible, with suitable immersion liquids, to obtain different apparent fiber densities for the same fiber. Furthermore, the differences in density values so obtained should vary in a manner related to the sizes of the liquid molecules used.

Such differences were not observed by Davidson because the liquids which he used were composed of molecules of approximately the same size. This fact is revealed in Table IV and Figure 7, in which the sizes of some liquid molecules used in density determinations are compared. (The dimensions are calculated from data compiled by Pauling [21].) All of these molecules except those of dioctyl phthalate and water are of approximately the same size.

It is not surprising, then, to observe an appreciable difference between the densities of porous textile fibers in benzene and dioctyl phthalate. The magnitude of this difference probably varies with the nature of the pore spaces within the fiber; although without some quantitative measure of porosity such an hypothesis would be difficult to check.

This brings us to a consideration of the effect that cutting the fibers has on the density values obtained for a given sample. If some of the porous channels within the fiber are not open either to the outside of the fiber or to the lumen, a greater density should be observed when the fiber is cut into short segments. The liquid can then enter some of those channels which are normally closed off. The amount of free space remaining within the fiber is thus reduced, and the observed density is correspondingly increased over that obtained for the whole fiber. The results given in Table III are in agreement with the above explanation.

Hermans [9], in his discussion of the structural significance of density values, argues that "by virtue of its biological origin and function, the system of

TABLE II. CHARACTERISTICS OF FIBERS USED IN DENSITY STUDY

Sample No.	Description	Staple length (in.)	Fineness* (μg./in.)	Maturity† (%)
1	Upland cotton	1	4.1	82
2	Upland cotton	$1\frac{1}{16}$	4.2	74
3	Wilds cotton	$1\frac{1}{4}$	3.8	77
4	"Memphis" immature cotton	$\frac{7}{8}$	2.8	28
5	Lockett 140 mature cotton	$\frac{7}{8}$	4.7	94
6	Absorbent cotton‡	—	4.9	—
7	Viscose rayon tow§	—	—	—

* Fineness determined by the Chicopee-Frazier Airflow Method.

† Percent mature fibers estimated by count of swelling and nonswelling fibers in 18% sodium hydroxide solution.

‡ Short-staple cotton which had been partially swollen and bleached in processing.

§ Cut viscose rayon tow of 1.52-den. filaments, average filament length 2.3 in.

TABLE III. DENSITIES OF FIBERS IN BENZENE, DIOCTYL PHTHALATE, AND MERCURY

Sample No.	Description	Density (g./cc.) Benzene	Dioctyl phthalate	Mercury
1	1-in. Upland cotton			
	Whole fibers	1.542	1.540	1.485
	Cut through 20-mesh screen	1.548	1.546	1.483
2	$1\frac{1}{16}$-in. Upland cotton			
	Whole fibers	1.540	1.526	1.481
	Cut through 20-mesh screen	1.575	1.557	1.478
	Cut through 40-mesh screen	—	1.543	—
	Cut through 60-mesh screen	1.544	1.539	—
	Cut through 60-mesh screen and boiled in water	—	1.541	—
3	$1\frac{1}{4}$-in. Wilds cotton			
	Whole fibers	1.539	1.498	—
	Cut through 20-mesh screen	1.558	1.532	—
4	$\frac{7}{8}$ in. "Memphis" immature cotton			
	Whole fibers	1.537	1.488	1.453
	Cut through 20-mesh screen	1.551	1.524	—
5	$\frac{7}{8}$-in. Lockett 140 cotton			
	Whole fibers	1.542	1.528	1.508
	Cut through 20-mesh screen	1.558	1.553	—
6	Absorbent cotton			
	Whole fibers	1.570	1.541	1.449
	Cut through 20-mesh screen	1.584	1.557	1.474
7	Viscose rayon			
	Whole filaments	1.511	1.516	1.486
	Cut through 20-mesh screen	1.516	1.519	1.512

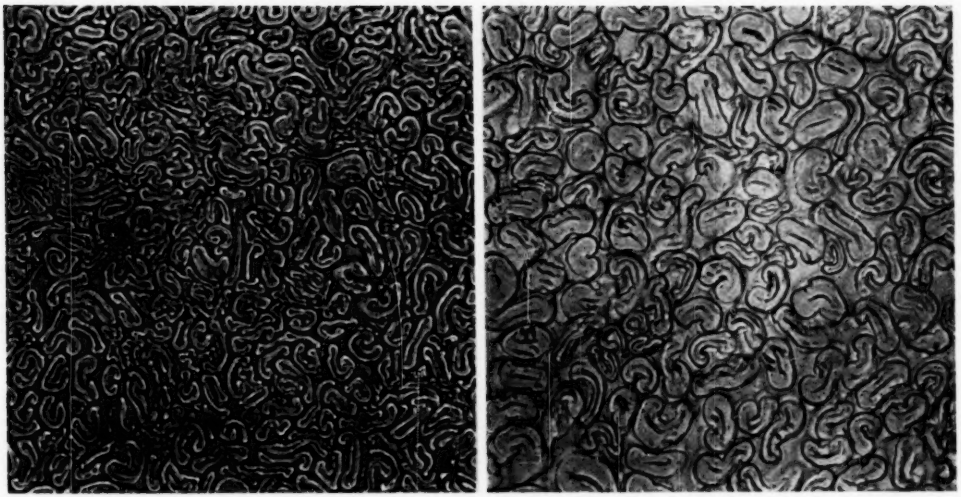

FIG. 6. *Photomicrographs of cross sections of immature and mature cotton fibers (Samples 4 and 5). (Magnification 400 ×.)*

capillaries occurring in native fibers will most probably be a continuous system in open communication with the outer world. It seems, therefore, reasonable to assume that the density of natural fibers, as determined in suitably chosen organic solvents, may be regarded as the true density of the proper substance of the fiber wall, or very nearly so." Proceeding from this assumption, Hermans concludes that the only free space in the fiber consists of small spaces between cellulose chains in noncrystalline cellulose regions. This conclusion is the basis of a calculation of the relative amounts of crystalline and noncrystalline cellulose in the cotton.

If the assumption proposed by Hermans is correct, then one should obtain the same density value for both the cut and the whole fiber. The noncrystalline cellulose exposed at the cut end is an insignificant fraction of the total noncrystalline portion present; and making the correspondingly small additional free space available to the liquid would hardly be expected to change the density by an appreciable amount. Yet the data of Table III indicate a greater apparent density for the cut fiber. Because Hermans' data were obtained on whole fibers only, it may be presumed that higher densities would have been

TABLE IV. ESTIMATED DIMENSIONS OF MOLECULES USED IN FIBER DENSITY MEASUREMENTS

Liquid	Shape	Length	Width	Thickness
Acetone	Angular	5.2Å.*	4.2Å.*	2.7Å.*
Benzene	Planar	5.5	5.5	1.5
Carbon tetrachloride	Spherical	5.5	5.5	5.5
Dioctyl phthalate	Planar	15.6	12.6	3.7
Heptane	Linear	10.2	3.7	3.7
Nitrobenzene	Planar	7.5	5.5	1.5
Toluene	Planar	7.1	5.5	1.5
Water	Angular	2.3	1.4	1.3

* Å. = Ångstrom unit, or 10^{-8} cm.

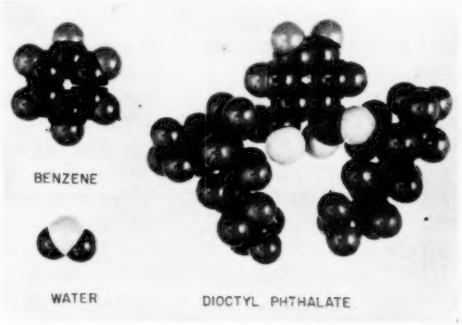

FIG. 7. *Photograph of scalar molecular models of dioctyl phthalate, benzene, and water, showing the relative sizes of the molecules.*

observed for cut samples. The density he reports may not necessarily, then, be a "true" density, and the estimates of crystallinity (or fractions of crystalline cellulose) based on such values are open to question.

It might be appropriate to consider briefly at this point the over-all fiber densities determined in mercury. Attention should be given to the fact that penetration of the mercury into the fibrous material is controlled by controlling the pressure upon the system. Thus, to determine the true over-all density of the fiber, a pressure which will cause mercury to penetrate the interfiber spaces but not the pores of the fiber itself must be selected. For this purpose, we have chosen the pressure at which the pressure *vs.* density curve has definitely leveled off—*viz.*, 165 p.s.i.a. At this pressure, it is calculated (using equation (1)) that all spaces larger than 1.7 microns in diameter will be filled with mercury. This diameter is about one-tenth that of the cotton fiber and slightly larger than that of the fiber lumen.

If the pressure selected above has been correctly chosen, the same density will be observed for both whole and cut cotton fibers. This is seen to be the case for Samples 1 and 2 at 165 p.s.i.a. (Table III). At higher pressures, the apparent density of the cut cotton increases, seemingly because the mercury begins to penetrate the fiber lumen. Theoretical calculations based on the elastic moduli of cellulose fibers indicate that fiber collapse or compressibility may also be a significant factor in this consideration. Microscopic observation, however, showed small mercury droplets still retained within some of the fiber lumen in fiber fragments which had been pressurized under mercury to 200 p.s.i.a. Hence, it was concluded that mercury had, at some stage of the measurement, penetrated some exceptionally large lumens of the cotton fiber.

The fact that densities of the cut absorbent cotton (Sample 6) and cut viscose rayon (Sample 7) are higher than those of the whole fibers is not so simply explained. For the rayon fibers, it might be postulated that when the fiber is in short segments the mercury penetrates its serrations to a greater extent than it does when the fiber is in long filaments. But this explanation cannot be applied to the absorbent cotton, which is a smooth-walled, partially swollen fiber.

The hypothesis that the absorbent cotton and rayon samples possess relatively large pores which are made accessible to the mercury by cutting the fibers also is not supported by microscopic observation and density data. For instance, the pressure-density curve of the cut rayon levels off at high pressures, much like the curve for the continuous filament. The full explanation of these results must await further study.

The density results described herein have still another important consequence in the study of fiber structure. It has been demonstrated that mechanical treatment such as ball milling decreases the crystallinity of cellulose fibers [12]. In an attempt to confirm this observation, Nelson and Conrad [20] noted that grinding (or cutting) cotton through a 2-mm. sieve in a Wiley mill caused a detectable reduction in degree of crystallinity, as indicated by the acid-hydrolysis technique. The treatment was identical with the cutting method employed in the density study herein reported.

It might be expected that if cutting the fiber decreases the cellulose crystallinity the density should be decreased correspondingly because the maximum density observed for cellulose should be that of the crystalline form. Actually, cutting the cotton through the 20-mesh screen results in a fiber of higher apparent density than that of the whole fiber. But this is true only for the mild cutting process, because cutting through 40-mesh or 60-mesh screens results in fiber fragments of considerably lower density in dioctyl phthalate than those cut through the 20-mesh screen (Sample 2, Table III). The reduction in crystallinity due to cutting or grinding of the fiber is thus confirmed by the density data, but the effect is apparently obscured when the fiber is subjected to mild cutting because of the increased accessibility of the immersion liquid to the inner parts of the fiber, which results in a higher apparent density.

From the density data obtained to date on the samples studied, an estimate of the volume of free (or noncellulosic) space within the fiber can be made. This volume is calculated by the formula

$$V_p = \frac{1}{D_f} - \frac{1}{D_c},$$

where V_p is the free volume in cubic centimeters per gram of dry fiber, D_f is the density of the fiber, and D_c is the crystalline density of cellulose. In applying this formula, we are assuming that the density of the cellulose chains is equal to the density of crystalline cellulose. The free-space volumes so calculated are shown in Table V.

TABLE V. ESTIMATED VOLUME OF FREE SPACE IN FIBERS CALCULATED FROM APPARENT DENSITY DATA

Sample No.	Description	Space volume in mm.³/g. of dry fiber inaccessible to: Benzene		Dioctyl phthalate		Mercury at 165 p.s.i.a.	
		Whole fiber	Cut fiber*	Whole fiber	Cut fiber*	Whole fiber	Cut fiber*
1	1-in. Upland cotton	21	18	22	19	46	47
2	1 1/8-in. Upland cotton	22	7	28	15	48	49
3	1 1/4-in. Wilds cotton	22	14	40	25	—	—
4	3/4-in. "Memphis" immature cotton	23	17	44	28	60	—
5	3/4-in. Lockett 140 mature cotton	21	14	27	16	35	—
6	Absorbent cotton	9	4	21	15	62	51
7	Viscose rayon	33	31	31	30	44	33

* Cut through a laboratory Wiley mill fitted with a 20-mesh screen.

Examination of the data calculated from densities of fibers in benzene shows that the volume of free space is larger in rayon than in cotton. This conclusion seems reasonable when it is recognized that the volume of space in the cotton lumen is not included in the values obtained from densities of the fibers in these liquids because the liquid fills the fiber lumen. The bubbles in the rayon filaments are probably not filled, according to the investigations of Hermans and Vermaas [10], and hence this bubble volume is included in the estimate of total free space for the rayon filaments.

If benzene, dioctyl phthalate, and mercury do not penetrate the pore spaces within the rayon filament, the volume of free space obtained with the three liquids should be the same. This was found to be approximately true. The somewhat larger space value observed with mercury must be attributed to the failure of this liquid to penetrate completely all the fiber serrations, even at the elevated pressure. Some of these serrations are seen from cross-section photomicrographs of the filaments to be very small. Some are less than a micron in width, small enough to prevent penetration of the mercury.

A study of the results given in Tables III and V reveals some interesting comparisons between the five raw cotton fibers investigated. Probably the most striking result is that all five fiber samples have the same apparent density values for the whole fiber in benzene. They have correspondingly identical free-space volumes. This result would lead one to suspect that the cotton cellulose wall is of constant density and is relatively impermeable to benzene. The differences in internal structure which may exist can be detected only by cutting the fiber to permit better access of the benzene.

Samples 1 and 2 are of about the same staple length, fineness, and maturity, yet their pore structures seem to be quite different. In Sample 1, about the same space is inaccessible to both benzene and dioctyl phthalate, even after the fiber has been cut. This result implies the existence of a fiber wall which neither liquid can penetrate. It indicates a channel system which may be entered not only through the cut fiber ends but also through the outside wall, if such a channel system does exist. The results for Sample 2, by way of contrast, indicate the existence of some spaces which are accessible to benzene but are not entered by the larger dioctyl phthalate molecule. Here there is apparently a channel system whereby the liquids can enter the wall better through the cut ends.

In the Wilds cotton (Sample 3), which is a finer, more mature cotton, the fiber wall is apparently full of holes through which the benzene, but not the dioctyl phthalate, can penetrate the cellulose substance. With dioctyl phthalate, the density is almost as low as that of the very immature cotton (Sample 4).

An interesting comparison can be made between the immature cotton (Sample 4) and the very mature (Sample 5) of the same staple length. The immature cotton is a low-density fiber with a great deal of free space, inaccessible to both benzene and dioctyl phthalate, and with a relatively large lumen. The mature Lockett cotton is a more compact fiber of

TABLE VI. VOLUMES OF FREE SPACE IN WATER-SWOLLEN CELLULOSE FIBERS AS ESTIMATED FROM HEAT-OF-FUSION DATA [15]

Maximum pore diameter →	190Å.*	570Å.*
	Free space volumes in cu. mm. per g. of fiber	
Cotton	72	126
Mercerized cotton	103	—
Rayon	130	200

* Å. = Ångstrom unit, or 10^{-8} cm.

somewhat higher density and with a relatively small lumen.

Finally, when a similar comparison of the effect of molecular size on apparent density is made with the absorbent cotton (Sample 6) and the viscose rayon (Sample 7), additional confirmation of the above explanation is obtained. In the preparation of absorbent cotton, the treatment swells the cellulose and opens up very small spaces within the fiber. The density of Sample 6 is therefore relatively high in benzene and considerably lower in dioctyl phthalate. In rayon, on the other hand, the spaces are small and isolated from one another; hence the densities in the two media are approximately the same.

It is interesting to compare the free-space values obtained for dry fibers by the density method with those obtained for similar wet fibers. Such values, calculated by Magne, Portas, and Wakeham [15] from heat-of-fusion data for wet cellulose, are shown in Table VI. These values were obtained by determining the weight of water within the fiber which failed to freeze at some temperature below 0° C, the normal freezing point of water. There is a direct relationship between the freezing point of water in small pore spaces and the size of the space—the smaller the pore, the lower the freezing point.

The data of Table VI indicate that there is more free space in water-swollen fibers than was found for similar dry fibers (Table V). This phenomenon is probably caused by two factors. First, the water molecule is much smaller than the benzene molecule, so that the water can penetrate more deeply into the cellulosic material. Second, water causes the fibers to swell and thus increases the size and volume of the pore spaces within the fiber. These factors are well known and lead one to expect the conclusions derived from a comparison of Tables V and VI.

Conclusions

It has been demonstrated that by proper choice of immersion liquid real differences in fiber densities can be observed. These differences are very probably related to the nature of the pore spaces within the fiber and may possibly be used to gain some information about the internal fiber structure. But a further investigation of densities, such as that outlined in this report, can be expected to yield only additional information of the same type. By using first benzene and then dioctyl phthalate we have fairly well covered the dimensional range of liquid molecules which are practical for density determinations by the method described above. Larger molecules exist only as solids or very viscous liquids at room temperature. Smaller molecules are either too volatile or too reactive with the cellulose material.

The basic problem in utilizing density measurements in fiber-structure investigation is to know and to *control* the extent of penetration of the liquid medium into the fiber. If the liquid is to wet the fiber, then some control may be obtained by proper selection of liquid molecules of suitable dimensions. With a nonwetting liquid, such as mercury, penetration is controlled by adjusting the pressure applied to the system. This second method theoretically shows more promise of yielding useful information about fiber structure than does the first.

The methods described have been applied to a study of different types of cotton fibers: raw, purified, swollen, and resin-treated. This continuation of the work at the Institute of Textile Technology was sponsored by the Office of Naval Research. The results obtained will be reported at a later date.

Acknowledgment

The author is pleased to acknowledge the assistance of Mr. Richard N. Taylor and Miss Nancy Spicer in the experimental work described. He is also indebted to Mr. C. H. Goldthwaite, of the Southern Regional Research Laboratory, U. S. Department of Agriculture, New Orleans, La., for the samples of immature and mature cotton (Samples 4 and 5).

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(Manuscript received June 24, 1949.)

Cottonseed Protein Fiber

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COTTONSEED MEAL AND CAKE amounting to about 2,000,000 tons annually represents a large potential source of industrial protein for use in the production of adhesives and fibers. With the development of the solvent-extraction industry for the removal of the oil from the cottonseed meats at low temperatures, the availability of meals containing unmodified and soluble proteins is increasing.

The utilization of cottonseed proteins obtained from solvent-extracted meals in the preparation of an artificial fiber has been retarded because of the difficulties encountered in isolating the protein from cottonseed meal, in dispersing the isolated protein in an aqueous medium in high concentration, and in preparing viscous and tacky dispersions.

The solubility in water of the proteins of cottonseed meal is much less than that of peanut or soybean proteins [6], indicating that the relative proportion of albumin to globulin components in cottonseed is less than it is in the meals of the aforementioned leguminous seeds. Consequently, cottonseed protein exhibits different properties from those of peanut or soybean protein when dispersions suitable for extruding into fiber are prepared. Burnett *et al.* [4] have reported that cottonseed protein is not completely soluble in alkali solutions having *p*H values from 11 to 12.8. They found it necessary to limit the concentration of protein in solutions to 12% to prevent gelling.

More recently, the laboratory-scale preparation and properties of viscous and tacky cottonseed protein dispersions with protein concentrations as high as 22% have been reported [1, 2, 5]. The laboratory-scale extrusion of relatively highly concentrated dispersions of cottonseed protein is reported here, together with some of the properties of the resulting fiber.

Experimental Procedures

Isolation of the Protein

Three methods for the isolation of protein from solvent-extracted cottonseed meal have been patented. In all three methods the meal is first washed with water to remove carbohydrate and other non-protein constituents. About 20% to 30% of the total nitrogen of the meal is removed during this washing.

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TABLE I. EFFECTS OF TOTAL MACHINE STRETCH AND AFTER-TREATMENT ON THE TENSILE PROPERTIES OF THE FIBER *

Fiber No.	Total stretch (%)	Denier† (g./9,000 m.)	After-treating bath (23°–27°C)	Tenacity‡ (g./den.) Conditioned	Tenacity‡ (g./den.) Wet	Elongation (%) Conditioned	Elongation (%) Wet
1	1,500	100	HCl 2% HCHO 5% NaCl 20%	0.74	0.20	28	47
2	430	135	HCl 2% HCHO 5% NaCl 20%	0.68	0.25	60	95
3	430	135	H_2SO_4 2%; HCHO 5% Na_2SO_4 15% Dextrose 15%	0.61	0.19	21	82
4	430	135	H_2SO_4 2% Na_2SO_4 15%	0.62	0.20	14	87
5	260	210	HCl 2% HCHO 5% NaCl 20%	0.67	0.30	61	98
6	260	210	H_2SO_4 2%; HCHO 5% Na_2SO_4 15% Dextrose 15%	0.63	0.25	42	108
7	260	210	HCHO 10%	0.57	0.24	5	103

* Coagulating bath contained 2% sulfuric acid, 15% sodium sulfate, and 15% dextrose at 23°–27°C; treating solution on No. 1 rolls contained 12% sodium chloride at 50°C; treating solution on No. 2 rolls contained 12% sodium chloride and 5% formaldehyde at 80°C.

† Properties determined on 40-filament yarn.

‡ Average of 10 tests, IP-2 Scott tester. The precision based on different preparations of fibers was ±0.03 g. per den.

According to two of the methods, the protein present in the meal is peptized in aqueous sodium hydroxide solutions at *p*H 10 to 11 and precipitated from the clarified extract by means of acid [3, 8]. In the third method the protein is peptized in 3% sodium chloride solutions and precipitated from the clarified extract by means of acid [9]. To improve the color of the isolated protein, Nickerson [8] suggested that the protein curd be washed and dried by means of acetone.

Oil-free cottonseed meal prepared by extracting the oil from flaked cottonseed meats with commercial hexane in a batch extractor [10] was used as the source of protein. This meal contained, on a moisture-free basis, about 9.5% of nitrogen, 1% of lipids, and 7.8% of ash.

The protein was extracted from the cottonseed meal by suspending the meal in water in the ratio 10 l. of water to 1 kg. of meal, and adjusting the *p*H of the suspension to 10 by means of sodium hydroxide. About 85% of the total meal nitrogen was soluble under these conditions. The extract liquor was clarified by screening, followed by passage through a super-centrifuge, and the protein was precipitated by adding gaseous sulfur dioxide to the extract liquor until the *p*H of the liquor was reduced to the isoelectric point of the protein—*i.e.*, *p*H 4. The curd was isolated from the mother liquor by centrifugation, washed several times with water and twice with acetone, and then air-dried. The isolated protein, which was light cream-colored in appearance, was obtained in a yield of about 30 to 35 weight percent. The protein contained, on a moisture-free basis, about 16.4% of nitrogen and 1.9% of ash.

An alternate method of extracting the protein to produce a protein of comparable fiber-forming properties involved suspension of the meal in a 0.1*M* sodium sulfite solution, clarification of the extract liquor, and precipitation of the protein by means of sulfur dioxide. The color of the isolated protein can be materially improved by carefully separating the hulls from the cottonseed meal.

TABLE II. EFFECT OF RATE OF LOADING ON THE TENSILE PROPERTIES OF MAN-MADE PROTEIN FIBERS *

Fiber	Tenacity, grams per denier				
	4-g. capacity	6-g. capacity	8-g. capacity	10-g. capacity	12-g. capacity
Cottonseed protein (laboratory preparation)	—	—	0.58	0.49	0.47
Peanut protein (laboratory preparation)	0.67	0.67	0.70	—	—
Peanut protein (commercial pilot plant)	—	1.19	1.27	1.08	—
Peanut protein (English pilot plant)	0.70	0.84	0.84	—	—
Casein (laboratory preparation)	—	1.12	1.15	0.95	—
Chicken feather (laboratory preparation)	—	—	0.79	0.72	0.63

* Single-fiber tests.

TABLE III. COMPARISON OF SOME MECHANICAL PROPERTIES OF COTTONSEED PROTEIN AND OTHER PROTEIN FIBERS *

Fiber sample	Young's modulus (g./den./%)	Load at 20% elongation (g./den.)	Tenacity at break (g./den.)	Elongation at break (%)
Cottonseed protein	0.12	—	0.58	5
Casein	0.16	0.88	1.15	49
Peanut protein (commercial pilot plant)	0.18	0.99	1.27	42

* Measured with an IP-2 Scott tester fitted with an 8-g.-capacity single-fiber attachment. Fibers conditioned at 65% relative humidity and 70°F.

Preparation of Protein Spinning Dispersions

Cottonseed protein, isolated by any of the methods described above, was suspended in water and 2.5% of trichloracetate ion on the basis of the weight of the protein was added, followed by the addition of 12%, on the basis of the weight of the protein, of sodium hydroxide in the form of a 50% aqueous solution. Lauric acid, 5% on the basis of the weight of the protein, was added either before or after the alkali to improve the tackiness of the dispersion. The dispersion was thoroughly agitated in a Waring blendor at a temperature maintained below 35°C. then deaerated by centrifugation. The deaerated dispersion was allowed to stand for about 2 hrs. at room temperature. The matured dispersions were tacky and had a viscosity of 75 to 100 poise.

Extrusion

The protein dispersion was extruded by means of a metering pump through a standard platinum-gold rayon spinneret having a 0.5-in. diameter face containing forty 0.1-mm. holds arranged in concentric circles. The details of the spinning machine have been previously described [7].

Methods of Testing the Fiber

The fibers were tested for tenacity and elongation after conditioning at 70°F (21°C) and 65% relative humidity. The tests were made on 10-in. lengths of filament yarn on an IP-2 Scott * tester equipped with a 250-g. carriage. Wet tests were made by first immersing the samples in water for 20 min., after which they were removed and immediately tested for wet strength and elongation.

Single-fiber tests were also made on 2-in. lengths of fiber on the IP-2 Scott tester equipped with a carriage whose capacity could be varied from 4 g. to 12 g. An electric static discharge marker was used to trace the load-elongation characteristics. Single-fiber tests were made only on conditioned but not wetted fibers.

Results

The effects of machine stretching and after-treatment of the wet coagulated fiber on the tensile properties of the conditioned fiber are shown in Table I.

* The use of firm names in this article is for identification and implies no endorsement of the manufacturer or the product.

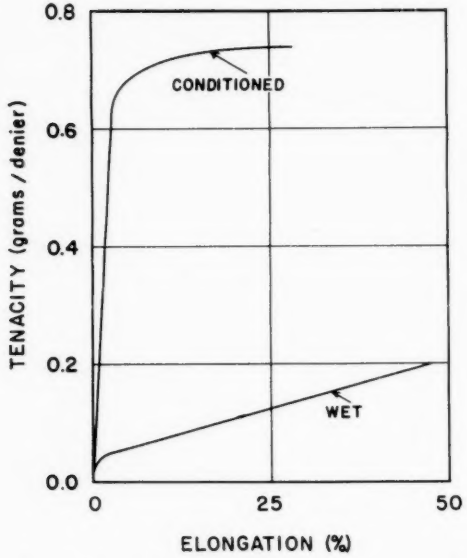

FIG. 1. *Load-elongation properties of cottonseed protein fiber.*

Comparing fibers 1, 2, and 5, it is observed that an increase in machine stretching resulted in a slight increase in the conditioned strength, a decrease in the wet strength, and a change in the elongation characteristics of the fiber. It may also be observed that the effect of after-treating with chloride ion resulted in an increase in the wet strength of the fiber.

Typical load-elongation curves for both conditioned and wet cottonseed protein fiber are shown in Figure 1. The weakness of the fiber in this preliminary stage of its development is indicated by the low yield point of the wet fiber.

The effect of rate of loading on the tensile properties of the fiber is shown in Table II. For the fiber samples which were compared the rate of loading represented by the 8-g.-capacity carriage gave a maximum value for the tenacity. Using this rate of loading the fiber, comparisons of some mechanical properties of the fiber are shown in Table III. It is observed that cottonseed protein fiber has a modulus comparable with the moduli of other man-made protein fibers.

Summary

The preparation of fibers from cottonseed protein has been described. These fibers have a dry strength of 0.6 to 0.7 g. per den. and a wet strength of 0.2 to 0.3 g. per den. They are yellow-to-orange color and have a soft hand.

Acknowledgment

The authors wish to thank W. S. Lewis and W. F. McSherry for determining the tensile properties of the fiber and Ruby K. Worner for her advice and interest in the work.

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(*Manuscript received July 1, 1949.*)

The Autoxidation of Alkali Cellulose

Part II*

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Abstract

The previous paper in this series discussed the uncatalyzed autoxidation of alkali cellulose and suggested that the reaction proceeds via a chain mechanism involving transient free radicals. The present paper describes the effect of certain transition metal catalysts on the kinetics of oxygen absorption and cellulose depolymerization. It is further shown that the reaction is subject to catalysis by substances which generate free radicals and by the presence of certain other autoxidizable substances. Silver and gold compounds behave as inhibitors, as do some typical organic antioxidants. The results provide further evidence for the free-radical chain character of the reaction. Possible depolymerization processes are discussed in terms of this approach.

Introduction

The previous paper in this series [7] considered various aspects of the kinetics and chemistry of the reaction between molecular oxygen and alkali cellulose. It showed that there was much evidence to suggest that this reaction proceeded by a chain mechanism in which free radicals were involved. In such reactions the highly active free radicals responsible for propagation of the chain process are present in extremely low stationary concentrations, and their presence is generally not capable of direct demonstration by, for example, measurements of paramagnetism, but must be inferred. There are many criteria which enable such inferences to be made [18, 21]. Oxidation processes involving radicals are subject both to catalysis by ions of the transition metals and to inhibition by a variety of substances in low concentration. They may be accelerated by addition to the system of molecules known to decompose, under the experimental conditions, with the production of free radicals. They may frequently be photosensitized and, where it can be measured, quantum yield is high.

In the present paper, a number of such criteria are applied to the autoxidation of alkali cellulose, and the results provide further strong evidence of the free-radical character of this reaction.

* Part I appeared in the September, 1949, issue of Textile Research Journal, page 527.

Effect of Traces of Various Added Metals

It has long been realized that various metals present in low concentration in alkali cellulose may exert a marked catalytic effect upon the rates of both autoxidation and depolymerization.

Wilson [5, 22] found that compounds of nickel, vanadium, cobalt, iron, cerium, manganese, and chromium, in decreasing order of magnitude, are positive catalysts, whereas lead is a strong inhibitor. Davidson [6] found iron, copper, and nickel to be positive catalysts and manganese to have a strong inhibitory action. Bartell and Cowling [2], on the other hand, showed that manganese increased both the rate of oxygen absorption and the amount of cellulose depolymerization resulting from a given absorption. Other workers [12, 17, 19] have confirmed the positive catalysis of iron and nickel, but have found copper to be without effect. The contradictions present in these various observations are reflected to some extent in work on other autoxidation reactions. Usually, the transition metals function as positive catalysts, but cases are known in which they may behave as inhibitors. Thus, copper stearate has been known to inhibit the cobalt or iron-stearate-catalyzed autoxidation of various hydrocarbons [8]. It is likely, therefore, that the relative efficiency of the metal as a chain initiator by a process such as:

$$ROOH + M^{\cdot} \longrightarrow RO^{\cdot} + {}^{\cdot}OH + M^{++} \quad (1)$$

TABLE I. EFFECT OF VARIOUS METALS ON THE RATE OF FLUIDITY INCREASE OF ALKALI CELLULOSE AT 20°C, P_{O_2}~740 MM. HG

Time (min.)	Fluidity (1% cellulose in cuprammonium) No added metal	0.0018% manganese	0.0016% iron	0.0020% cobalt	0.0014% nickel	0.0043% silver	0.0400% gold
0	5.7	6.4	6.2	8.3	6.8	5.2	5.0
1,440	13.2	16.7	14.9	22.7	14.5	5.4	10.7
2,880	18.6	22.3	21.2	31.6	20.6	10.7	13.5
4,320	23.0	25.7	25.3	36.8	24.9	14.9	17.2
5,760	26.0	29.5	28.5	38.9	29.1	—	17.8
7,200	29.5	34.1	32.1	41.8	30.2	—	19.0

or as a chain terminator by:

$$RO— + M^{+} \longrightarrow RO^{-} + M^{++} \qquad (2)$$

$$—OH + M^{+} \longrightarrow OH^{-} + M^{++} \qquad (3)$$

determines its catalytic or antioxidant activity.

If the metal is to retain its activity, then reactions which result in reduction of the oxidized cation must also occur. These will, in general, be simple oxidation processes; *e.g.*,

$$RO^{-} + M^{++} \longrightarrow RO— + M^{+},$$

likely to result in radical formation.

In the work described here, an attempt was made to obtain further information on the mode of action of metals catalytically active in the autoxidation of alkali cellulose. A rough "sorting test" of the catalytic activity of a number of metals of variable valency was first carried out in order to obtain an independent evaluation of those producing catalysis sufficiently marked to justify further kinetic study. The metals were incorporated into alkali cellulose, of the composition normally used in the viscose industry and prepared as previously described [7], by the addition of suitable compounds to the steeping solution. In the majority of cases metallic hydroxides are sufficiently soluble in 5.5*N* sodium hydroxide solution to give a resultant alkali cellulose containing up to 0.002% of the metal. The alkali celluloses so produced were aged in oxygen at atmospheric pressure in a 20°C thermostat. Samples were removed at suitable intervals for determination of the cuprammonium fluidity of the cellulose content. Results of this experiment are given in Table I. They show that nickel, iron, manganese, and cobalt, in that order, are increasingly effective positive catalysts at concentrations of the order of 0.002% in alkali cellulose and that, interestingly, gold and silver in higher concentrations behave as inhibitors.

The effects of manganese and cobalt on the kinetics of oxygen absorption at constant pressure were next studied and results are given in Figures 1, 2, and 3 and in Table II. It is clear that when these metals are present in concentrations below 0.002% they do not affect the initial rate of autoxidation but cause the subsequent rate to increase progressively relative to that of the comparison material containing no added metal.

These results provide strong evidence for the suggestion, already made with reference to other autoxidation processes [8, 16], that the catalytic effect of the transition metals is related not to the primary reaction but to the secondary process of slow chain branching which they accelerate, presumably by catalyzing the decomposition of the organic hydroperoxides formed by the chain reactions already postulated. It has been suggested [16] that the equation

$$ROOH + M^{+} \longrightarrow RO^{\cdot} + —OH + M^{++} \qquad (1)$$

may account for such catalyzed chain branching. An experiment, not reported here, showed that a trace of ethylene diamine inhibited completely the catalytic activity of cobalt. It is well known that ethylene diamine forms a complex with trivalent cobalt and thereby stabilizes the cobalt ion in this valency state. The observation confirms the impression that reversibly variable valency at a suitable potential is a prerequisite for a metallic catalyst of this reaction.

Reference to Figure 4 shows that in the presence of 0.0051% cobalt the measurable changes in the cellulose fluidity, its aldehyde-group content, and its carboxyl-group content, produced by a given oxygen absorption, are notably greater than when cobalt is absent. Davidson [6] observed that catalysis by iron had a similar but less marked effect with respect to fluidity and copper number, whereas Bartell and Cowling [2] reported that the presence of manganese

TABLE II

Effect of Various Metals on the Rate of Autoxidation of Alkali Cellulose at 25°C and $P_{O_2} \simeq 700$ mm. Hg

Metal content of alk. cell.	Time (min.)	$10^2 \times$ velocity coefficient ((n.t.p.) ml. O_2/g. cell./min.)
0.000% cobalt	47	1.49
	369	1.20
	1,396	0.82
	1,818	0.863
	2,831	0.68
	4,000	0.67
0.0004% cobalt	191	1.36
	1,275	1.32
	1,695	1.10
	2,756	1.10
	3,155	1.05
0.0010% cobalt	57	1.29
	258	1.35
	1,380	1.94
	1,780	2.22
	2,834	1.98
	3,240	1.96
0.0029% cobalt	55	1.26
	386	1.55
	1,386	2.59
	1,841	2.79
	2,860	2.79
	4,000	2.50
0.000% manganese	47	1.49
	369	1.20
	1,396	0.82
	1,817	0.86
	2,831	0.68
	4,000	0.67
0.0032% manganese	90	1.49
	306	1.48
	1,678	1.49
	3,112	1.52
0.015% manganese	80	1.12
	1,195	0.84
	2,687	0.80
	4,015	0.74
0.25% manganese	60	2.26
	400	1.46
	1,401	0.64
	2,875	0.15
	4,280	0.23
0.62% manganese	30	1.98
	280	1.21
	1,140	0.50
	2,640	0.19
	3,840	0.17

Effect of Various Metals on the Rate of Fluidity Rise of Alkali Cellulose at 25°C and $P_{O_2} \simeq 700$ mm. Hg

Metal content of alk. cell.	Time (min.)	Fluidity (1 % solution)
0.000% cobalt	0	6.1
	100	7.2
	200	8.4
	300	9.5
	400	10.4
	500	11.4
	600	12.4
0.0010% cobalt	0	7.6
	30	8.4
	60	9.5
	90	10.6
	120	11.3
	150	12.8
	180	13.4
0.0024% cobalt	0	7.6
	30	10.3
	60	12.5
	95	14.2
	125	15.3
	185	16.6
0.000% manganese	35	7.30
	290	8.28
	1,235	18.4
	2,700	26.0
0.0032% manganese	0	8.5
	760	17.0
	2,560	28.1
0.015% manganese	0	9.05
	1,290	15.9
	2,670	21.5
	4,050	24.0
0.25% manganese	0	14.8
	1,260	17.25
	2,760	17.90
0.62% manganese	0	8.0
	1,140	8.0
	2,580	8.7
	3,920	9.4

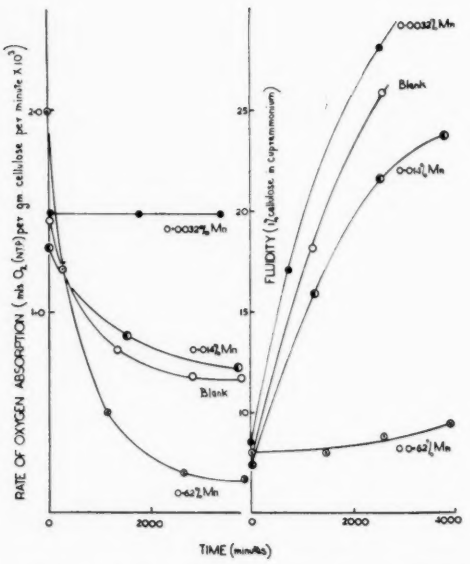


FIG. 1. *The effect of added manganese on the autoxidation characteristics of alkali cellulose (at 25°C and P_{O_2} = 700 mm. Hg).*

(NOTE: "0.014% Mn" should be "0.015% Mn" for the two curves.—*Editor.*)

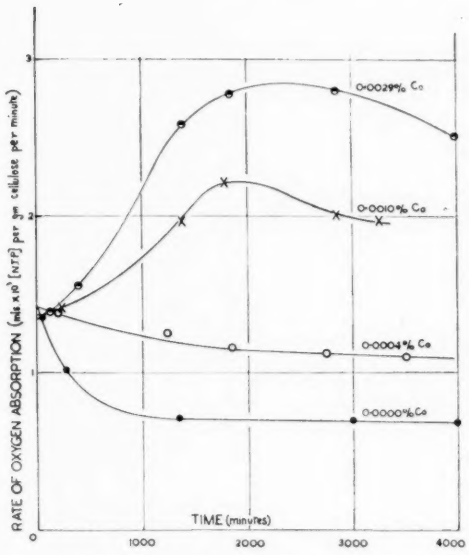


FIG. 2. *The effect of cobalt on the rate of autoxidation of alkali cellulose at 25°C and P_{O_2} = 700 mm. Hg (pulp No. 2). (Cobalt concentrations calculated on alkali cellulose.)*

produced a greater change in fluidity for a given oxygen absorption. It may be tentatively accepted, then, that the phenomenon is a general one for cases of marked catalysis of the autoxidation of alkali cellulose by the transition metals.

Figure 5 compares at various temperatures the effect of cobalt concentration on the time required for the fluidity of cellulose to increase from 6 initially to an arbitrary value of 20 (1% cellulose in cuprammonium). It is clear that the catalytic effect of cobalt on this aspect of the reaction increases rapidly as its concentration varies from 0 to 0.002% on the alkali cellulose and that higher concentrations of cobalt have little additional effect. Bartell and Cowling's results show that manganese catalysis of the reaction has a similar concentration relationship. The results given in Figure 5 also suggest that the catalytic activity of cobalt increases with increasing temperature. Thus the maximum catalysis observed at 20°C reduced the arbitrary reaction time to approximately 31% and at 35°C to 14% of its uncatalyzed value. The 30°C result was intermediate at 20%.

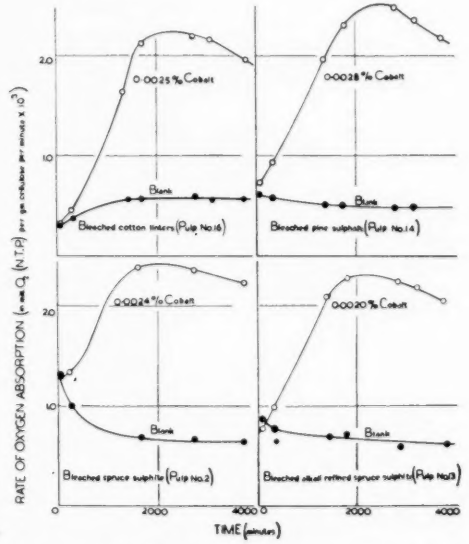

RATE OF OXYGEN ABSORPTION (= mls O_2 (NTP) per gm cellulose per minute X 10^3)
0·0025% Cobalt
0·0028% Cobalt
0·0024% Cobalt
0·0020% Cobalt
Blank
Bleached cotton linters (Pulp No.16)
Bleached pine sulphate (Pulp No.14)
Bleached spruce sulphite (Pulp No.2)
Bleached alkali refined spruce sulphite (Pulp No.3)
TIME (minutes)

FIG. 3. *The effect of cobalt on the autoxidation characteristics of alkali celluloses produced from various commercial pulps (at 25°C and P_{O_2} = 700 mm. Hg).*

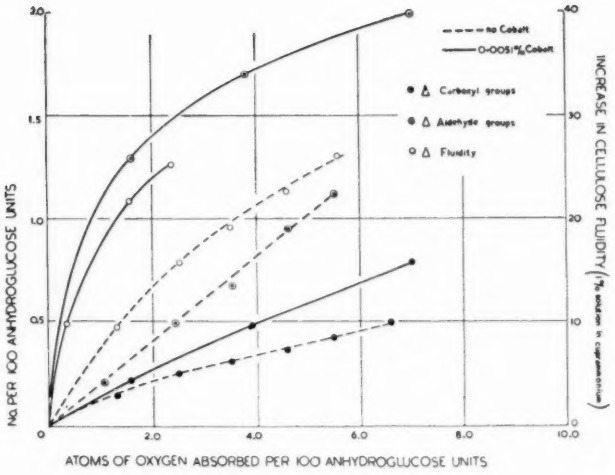


FIG. 4. *The effect of cobalt on the relation between oxygen consumption and changes produced in cellulose during the autoxidation of alkali cellulose (at 25°C and $P_{O_2} = 700$ mm. Hg).*

The apparent contradiction between the results of Davidson [6] and of Bartell and Cowling [2] does not necessarily exist. The former found that manganese when present in concentrations of the order of 0.05–0.1% was a strong inhibitor, whereas the latter showed that a positive catalytic effect obtained at manganese concentrations of below 0.005%. Preliminary results obtained by the present authors and illustrated in Figure 1 indicate that the catalytic effect of manganese reaches a maximum at a concentration of about 0.0025% and thereafter falls off, becoming negative at the high concentrations used by Davidson. The higher concentrations of manganese —*i.e.*, 0.015%, 0.25%, and 0.62% on the alkali cellulose—were added to the original cellulose (pulp No. 2 of Part I of this series [7]) by steeping this successively in aqueous solutions of manganous sulfate and dilute sodium hydroxide, followed by washing and drying. The high initial fluidity of the sample containing 0.25% manganese may be due to induced autoxidation of the cellulose consequent upon the autoxidation of manganous hydroxide in contact with it.

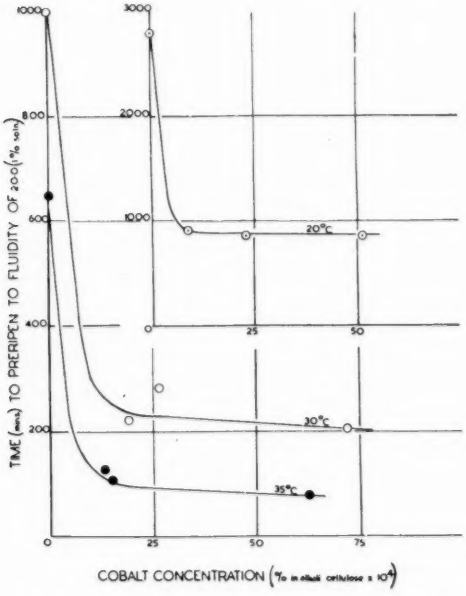


FIG. 5. *The effect of cobalt concentration in alkali cellulose on the time required to pre-ripen to a fluidity of 200 (1% solution) in oxygen at various temperatures ($P_{O_2} = 700$ mm. Hg).*

The preliminary sorting experiment, described above, showed that the incorporation of gold and particularly of silver in alkali cellulose had a marked inhibitory effect on the rate of fluidity rise during autoxidation. This effect is emphasized by the results given in Table III and in Figures 6, 7, and 8. It is clear that:

1. The presence of silver has comparatively little, or perhaps no, effect on the initial rate of autoxidation, but it strongly depresses that rate during subsequent stages of the reaction.

TABLE III. EFFECT OF SILVER ON THE AUTOXIDATION CHARACTERISTICS OF ALKALI CELLULOSE AT 25°C, P_{O_2} = 700 MM. HG

Pulp	Silver content of alk. cell.	Time (min.)	$10^3 \times$ velocity coefficient (ml. O_2/g./min. (n.t.p.))	Volume of oxygen absorbed (ml./g. cell. (n.t.p.))	Fluidity (1% solution)
Bleached spruce sulfite (Pulp No. 2)	0.000%	34	1.345	0.0	6.1
		266	1.01	0.5	10.6
		1,337	0.686	1.0	17.1
		1,699	0.700	1.5	21.7
		2,780	0.700	2.0	25.7
		4,268	0.642		
	0.0018%	63	1.46	0.0	4.5
		321	0.568	0.5	7.7
		1,392	0.276	1.0	11.8
		1,744	0.276	1.5	16.9
		3,190	0.227		
		4,314	0.218		
		4,643	0.216		
		5,765	0.193		
		8,618	0.148		
	0.0043%	40	0.864	0.0	5.2
		333	0.627	0.5	5.5
		1,371	0.339	1.0	9.0
		1,765	0.275	1.5	14.9
		2,800	0.240		
		3,175	0.249		
		4,237	0.183		
		4,611	0.212		
		5,670	0.179		
		6,040	0.186		
		7,122	0.166		
		8,000	0.141		
	0.0500%	35	0.936	0.0	4.6
		1,035	0.393	0.5	4.8
		1,413	0.307	1.0	5.1
		2,503	0.173	1.5	6.0
		2,856	0.173		
		3,940	0.118		
		4,325	0.114		
		4,800	0.070		

2. Small concentrations of silver reduce and higher concentrations inhibit almost completely the cellulose depolymerization resulting from the reaction.

3. Increasing concentrations of silver reduce progressively the amount of depolymerization which results from a given oxygen absorption.

The strong red coloration of the alkali cellulose to which gold had been added as chloroaurate in the steeping solution suggested that some (at least) of this compound had been reduced and that metallic gold in colloidal form was present. A similar conclusion appeared to be likely in the case of silver, but here the evidence was less definite on account of the strong color of silver oxide. It is interesting to note that Berl and Winnaker [3] found that colloidal dispersions of metallic iron, tin, and lead strongly inhibited the autoxidation of benzaldehyde, whereas, less obviously relevant, Hinshelwood and others [10] noted that a silver reaction vessel had some inhibiting effect on the hydrogen-oxygen reaction. The general reaction appears to be one of radical chain termination, perhaps an electron-transfer reaction of the type

$$\text{—OH} + \text{M} \longrightarrow \text{OH}^- + \text{M}^+.$$

The colloidal metals are also likely to decompose hydrogen peroxide heterogeneously by a reaction which presumably does not involve free radicals.

TABLE III—*Continued*

Pulp	Silver content of alk. cell.	Time (min.)	$10^3 \times$velocity coefficient (ml. O_2/g./min. (n.t.p.))	Volume of oxygen absorbed (ml./g. cell. (n.t.p.))	Fluidity (1% solution)
Bleached cotton linters (Pulp No. 16)	0.000%	45	0.307	0.0	6.3
		325	0.379	0.5	13.8
		1,432	0.570	1.0	19.6
		1,772	0.570	1.5	25.1
		2,851	0.602		
		2,199	0.560		
		4,345	0.564		
		4,643	0.566		
	0.0018%	55	0.266	0.0	8.1
		272	0.285	0.5	11.2
		1,343	0.312	1.0	15.3
		1,669	0.313	1.5	18.0
		2,815	0.329		
		3,136	0.328		
		4,288	0.311		
		8,000	0.218		
	0.0045%	55	0.404	0.0	7.2
		362	0.394	0.5	13.6
		1,396	0.345	1.0	18.5
		1,761	0.359	1.5	22.5
		2,835	0.355	2.0	26.0
		5,754	0.334		
		6,083	0.320		
		7,205	0.309		
	0.0220%	60	0.284	0.0	6.7
		306	0.215	0.5	8.0
		1,424	0.110		
		1,752	0.107		
		2,823	0.079		
		3,149	0.077		
		4,295	0.053		
		4,616	0.037		
		5,768	0.042		
		8,000	0.020		

Figure 13 of the previous paper [7] shows that the incorporation of silver in alkali cellulose reduces the stationary peroxide concentration effectively to zero. It should also be noted that silver oxide is a useful preparative oxidizing agent capable, for example, of oxidizing aldehydes to carboxylic acids and, in the present case, perhaps of diminishing the concentration of active, autoxidation chain-starting, reducing groups. In this respect the results given in Figure 8 are interesting.

Effect of Introducing Substances Which Generate Free Radicals

Many reactions, both autoxidations and polymerizations, which are known to proceed by free-radical-propagated chain mechanisms may be accelerated by the addition of substances which decompose homolytically to produce free radicals. Thus, vinyl polymerization is catalyzed by dibenzoyl peroxide [9], whereas triphenylmethyl [23] promotes the autoxidation of various aldehydes. It was thought that the autoxidation of alkali cellulose might be accelerated in the presence of such materials, and further evidence for the free-radical character of this reaction obtained thereby.

The range of substances soluble in 5.5*N* NaOH which are likely to generate free radicals is rather limited. In the experiments described here, only benzene diazonium hydroxide and ammonium persulfate were used. The former is considered to un-

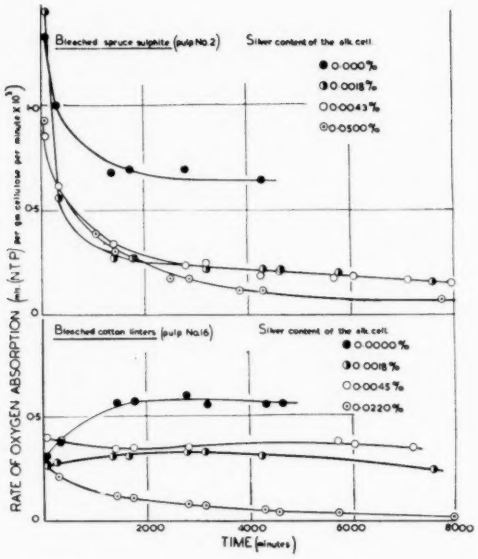


FIG. 6. *The effect of silver on the autoxidation characteristics of alkali cellulose (at 25°C and* $P_{O_2} = 700$ *mm. Hg).*

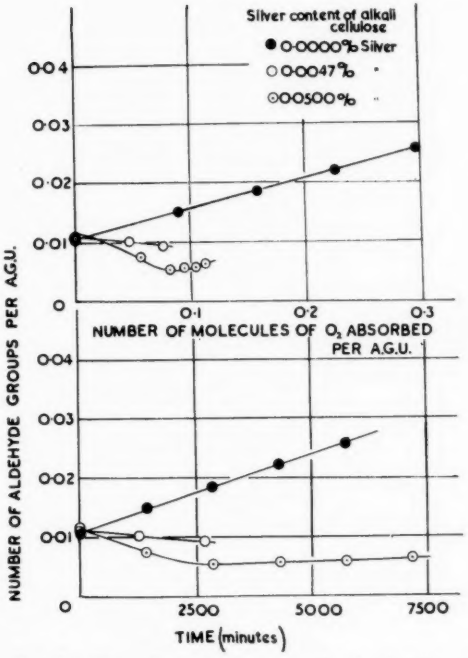


FIG. 8. *The effect of silver on the production of aldehyde groups during the autoxidation of alkali cellulose (at 25°C and* $P_{O_2} = 700$ *mm. Hg).*

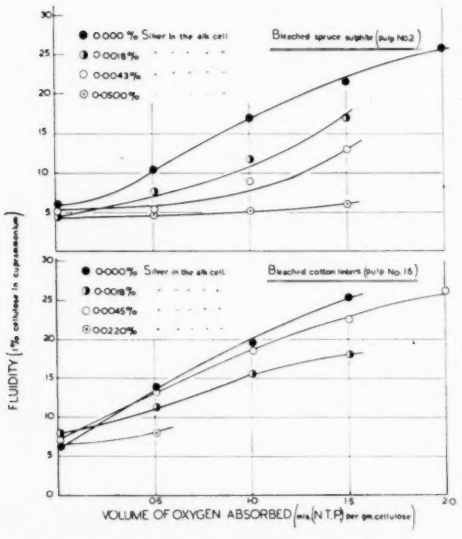

● 0·000% Silver in the alk cell
◑ 0·0018%
○ 0·0043%
⊙ 0·0500%
Bleached spruce sulphite (pulp No.2)
● 0·0000% Silver in the alk cell
◑ 0·0018%
○ 0·0045%
⊙ 0·0220%
Bleached cotton linters (pulp No.16)
FLUIDITY (1/% cellulose in cuprammonium)
VOLUME OF OXYGEN ABSORBED (mls (N.T.P) per gm cellulose)

FIG. 7. *The effect of silver on the relation between fluidity rise and oxygen consumption during autoxidation of alkali cellulose (at 25°C and* $P_{O_2} = 700$ *mm. Hg).*

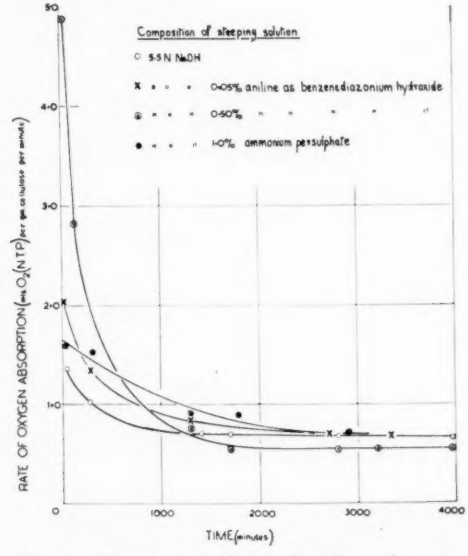

Composition of steeping solution
○ 5·5 N NaOH
× " " 0·05% aniline as benzendiazonium hydroxide
⊗ " " 0·50% " " " " "
● " " 1·0% ammonium persulphate
RATE OF OXYGEN ABSORPTION (mls O₂ (N.T.P) per gm cellulose per minute)
TIME (minutes)
1000
2000
3000
4000

FIG. 9. *The effect of "free radicals" on the rate of autoxidation of alkali cellulose (at 25°C and* $P_{O_2} = 700$ *mm. Hg).*

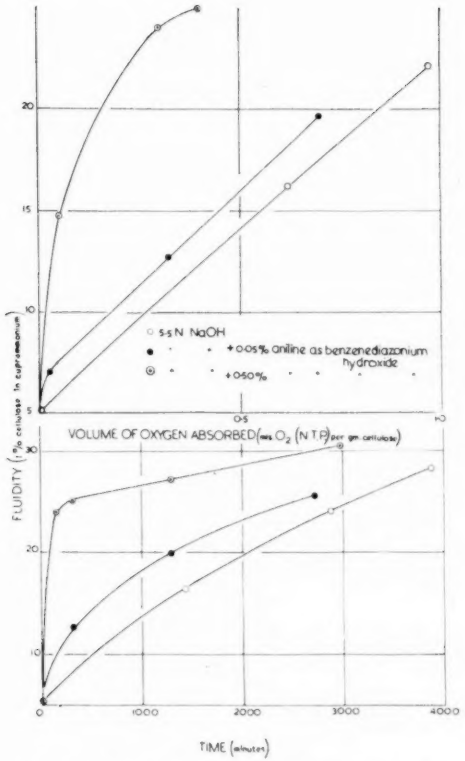

5·5 N NaOH
+0·05% aniline as benzenediazonium hydroxide
+0·50% " " "
VOLUME OF OXYGEN ABSORBED (mls. O2 (N.T.P.) per gm. cellulose)
FLUIDITY (1/% cellulose in cuprammonium)
TIME (minutes)

FIG. 10. *The effect of "free radicals" on the autoxidation of alkali cellulose (at 25°C and* $P_{O_2} = 700$ *mm. Hg).*

dergo decomposition to produce initially free phenyl and hydroxyl radicals [21]:

$$Ph{-}N_2{-}OH \longrightarrow Ph{-} + N_2 + {-}OH.$$

Ammonium persulfate was found, experimentally, to oxidize cellulose under strongly alkaline conditions, and it has been suggested [14] that transient molecular species of a free-radical character occur during persulfate oxidations.

These two substances were incorporated in alkali cellulose by their addition to the sodium hydroxide steeping solution. Rates of autoxidation and of fluidity increase were measured as previously described. Benzenediazonium hydroxide decomposes fairly rapidly in 5.5*N* NaOH, and blank experiments carried out in the absorptiometer in the absence of oxygen showed that after the alkali cellulose reached

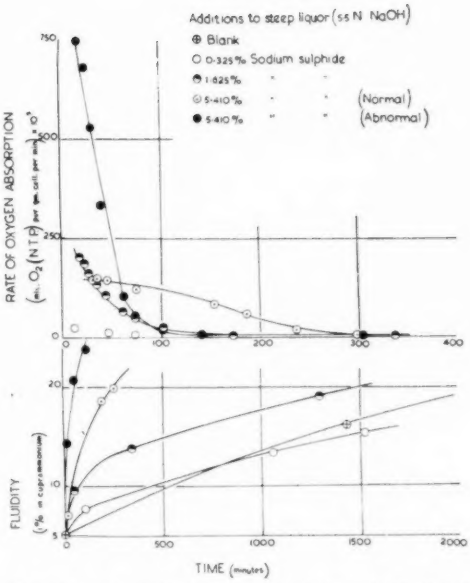


FIG. 11. *Autoxidation characteristics of alkali cellulose containing sodium sulfide (at 25°C and* $P_{O_2} = 700$ *mm. Hg).*

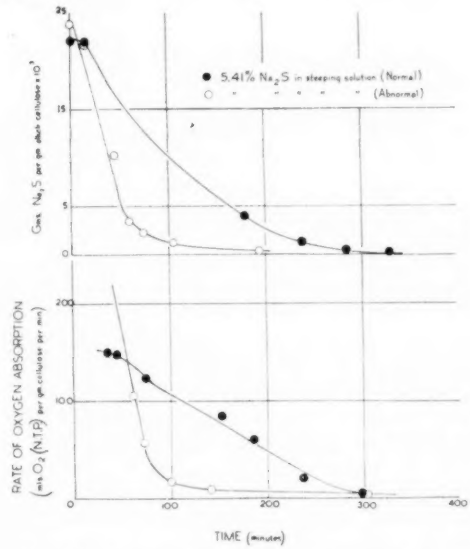

● 5·41% Na2S in steeping solution (Normal)
○ " " " " (Abnormal)
Grms. Na2S per gm. alkali cellulose × 10³
RATE OF OXYGEN ABSORPTION
TIME (minutes)

FIG. 12. *Relation between rate of oxygen absorption and sodium sulfide concentration during autoxidation of alkali cellulose containing sodium sulfide (at 25°C and* $P_{O_2} = 700$ *mm. Hg).*

TABLE IV. EFFECT OF SUBSTANCES GENERATING FREE RADICALS ON THE AUTOXIDATION OF ALKALI CELLULOSE

Composition of steeping solution	Time of reaction (min.)	Rate of autoxidation at 25°C and P_{O_2} = 700 mm. Hg ($10^3 \times$ ml. O_2 at n.t.p. absorbed per g. cell. per min.)	Total volume of oxygen absorbed (ml. O_2 per g. cell.)	Cellulose fluidity (as 1% solution in cuprammonium)
5.5*N* NaOH	0	—	0	5.0
	34	1.35	0.06	—
	266	1.01	0.31	7.3
	1,337	0.69	1.16	16.2
	1,699	0.70	1.41	—
	2,780	0.70	2.10	23.4
	4,268	0.64	3.10	28.3
5.5*N* NaOH + 0.05% aniline as benzenediazonium hydroxide	0	—	0	(5.0)
	15	2.01	0.05	7.0
	140	1.35	0.34	10.0
	1,345	0.82	1.45	19.8
	2,850	0.71	2.19	26.0
	3,180	0.71	2.38	—
5.5*N* NaOH + 0.5% aniline as benzenediazonium hydroxide	0	—	0	(5.0)
	28	4.87	0.17	17.0
	125	2.82	0.54	23.4
	1,300	0.76	1.90	27.0
	1,715	0.54	2.15	—
	2,785	0.54	2.75	30.1
	3,150	0.56	2.94	—
	4,155	0.50	3.46	—
5.5*N* NaOH + 1% ammonium persulfate	0	—	0	5.0
	19	1.57	0.03	8.2
	356	1.56	0.56	15.7
	1,320	0.91	1.76	21.8
	1,816	0.91	2.17	—
	2,963	0.66	2.98	28.0

this apparatus no measurable volume of nitrogen was evolved to interfere with determination of rates of autoxidation. The observed effects were therefore due to very low concentrations of the active molecular species. It is shown later (see Table VI), that both phenol and sodium nitrite are without substantial effect upon the autoxidation of alkali cellulose, and the results here may therefore reasonably be attributed to very low concentrations of phenyl or hydroxyl radicals in the system. These results are given in Table IV and Figures 9 and 10.

Benzenediazonium hydroxide increases both the initial rates of autoxidation and of fluidity rise and, as shown in Figures 10 and 16, it increases the amount of cellulose depolymerization which results from a given consumption of oxygen. Under the present experimental conditions these effects decrease rapidly with increasing reaction time and are negligible after 400 minutes' reaction, presumably on account of the rapid disappearance of the active molecular species. The presence of ammonium persulfate increases the autoxidation rate over a longer period. In this case no useful conclusions can be drawn from the fluidity measurements since ammonium persulfate itself may oxidize cellulose.

Effect of Addition of Various Autoxidizable Materials and Antioxidants

The introduction into an autoxidizing system of a second substance which can itself be autoxidized may result in either acceleration or retardation of the main reaction. Thus, the autoxidation of nitrites and arsenites may be induced by the addition of sodium sulfite, although sodium sulfite inhibits the autoxidation of benzaldehyde [21]. Other, less readily oxidizable substances also behave as antioxidants—*e.g.*, benzoquinone and anthraquinone strongly inhibit the autoxidation of anethole [13]. Such materials may perhaps function as hydrogen-atom donors, terminating radical chains by substituting a more

TABLE V. Effect of Sodium Sulfide on the Rates of Oxygen Absorption and of Depolymerization of Alkali Cellulose (Pulp No. 2) at 25°C and 700 mm. Hg

Composition of steeping solution	Time of reaction (min.)	Rate of oxygen absorption (ml. O_2(n.t.p.) per g. cell./ min. $\times 10^2$)	Cellulose fluidity (1% solution in cuprammonium)	Sodium sulfide content of alk. cell. (g. Na_2S/g. alk. cell.)
5.5*N* NaOH	0	—	5.0	—
	34	1.35	—	—
	266	1.01	7.3	—
	1,337	0.69	16.2	—
	1,699	0.70	—	—
	2,780	0.70	23.4	—
5.5*N* NaOH + 0.325% Na_2S	0	—	(5.0)	—
	23	25.4	—	—
	47	14.6	6.3	—
	74	6.4	7.2	—
	1,044	0.58	14.0	—
5.5*N* NaOH + 1.62% Na_2S	0	—	(5.0)	—
	17	203	—	—
	27	161	—	—
	44	108	9.6	—
	102	24.9	11.1	—
	338	1.4	14.0	—
	1,016	0.60	17.5	—
5.5*N* NaOH + 5.41% Na_2S (normal)	0	—	(5.0)	0.0220
	35	149	10.5	—
	75	123	13.9	0.0126
	154	84.5	—	0.0056
	237	20.5	20.0	0.0013
	298	5.1	21.4	0.0004
5.5*N* NaOH + 5.41% Na_2S (abnormal)	0	—	(5.0)	0.0237
	16	746	15.9	0.0201
	30	528	18.5	0.0135
	62	105	21.4	0.0035
	100	16.7	—	0.0013
	141	8.9	24.5	0.0006
	303	3.6	—	—

stable radical for the highly reactive chain-propagating species. The present discussion deals with both these types of phenomena as they occur during alkali cellulose autoxidation. The special case of inhibition of the reaction by silver and gold has already been discussed.

It has been reported [4] that the addition of sodium sulfide to alkali cellulose has been used industrially to accelerate the pre-ripening process, and various workers [11, 15] have discussed the effect. Results given here (Tables V and VI) show that of all the autoxidizable materials investigated sodium sulfide is outstanding in its effect upon alkali cellulose autoxidation.

In Table V and Figures 11 and 12 the effects of adding sodium sulfide to the steeping solution on both the rates of oxygen absorption and of cellulose depolymerization are shown. During autoxidation the sodium sulfide is destroyed and its effects upon alkali cellulose persist only so long as it is present in appreciable concentration. The magnitude of these effects increases roughly with increasing initial sodium sulfide content. It was found, however, that at the highest sulfide concentration employed the measured rates of reaction were not entirely reproducible. Two series of rates were obtained, the slower recorded as normal and the faster as abnormal in Table V and Figures 11 and 12. Strangely enough, no intermediate rates were obtained, and it was considered that the abnormal results were due to the adventitious presence of a trace of some other material which was a positive catalyst for sodium sul-

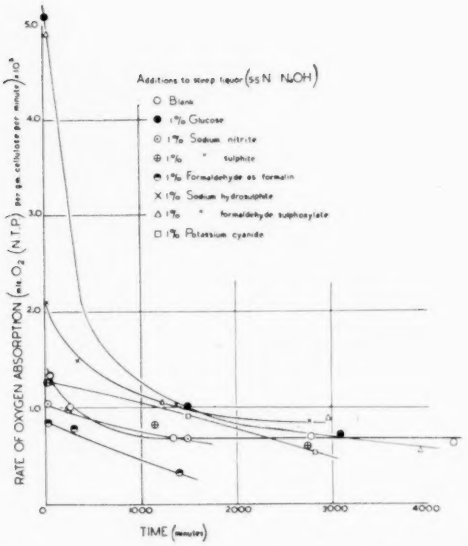

Additions to steep liquor (5.5 N NaOH)
○ Blank
● 1% Glucose
⊙ 1% Sodium nitrite
⊕ 1% " sulphite
◓ 1% Formaldehyde as formalin
× 1% Sodium hydrosulphite
△ 1% " formaldehyde sulphoxylate
□ 1% Potassium cyanide
RATE OF OXYGEN ABSORPTION (ml O2 (N.T.P.) per gm cellulose per minute) ×10³
TIME (minutes)

FIG. 13. *The effect of various oxidizable substances on the autoxidation of alkali cellulose.*

fide autoxidation. In the present experiments no clue was obtained as to the identity of this catalyst. Experiments, not recorded here, showed that sodium sulfide alone, in 5.5*N* NaOH, autoxidizes at an appreciable rate at room temperature. This reaction shows the initial induction period characteristic of many autoxidation processes. Unlike the autoxidation of sodium sulfite, which has been so much studied, and established as a radical chain reaction [11], there is apparently no reference in the literature to the mechanism of sulfide autoxidation. Presumably, however, this proceeds by a similar mechanism and it seems reasonable to suppose that transient free radicals, produced thereby, are capable of dehydrogenating cellulose and so accelerating its autoxidation under alkaline conditions.

A further series of experiments was carried out in which various other substances, likely to be autoxidized under the experimental conditions, were incorporated in alkali cellulose by their addition in 1% concentration to the steeping solution. Table VI and Figures 13 and 14 show the effect of these substances on both autoxidation and depolymerization rates. Of the materials studied, only glucose, sodium formaldehyde sulfoxylate, and sodium hydrosulfite increased the rate of oxygen absorption and only sodium formaldehyde sulfoxylate had any significant effect upon the rate of cellulose fluidity rise. This effect was, however, not comparable in magnitude with that of sodium sulfide. Formaldehyde showed a pronounced antioxidant activity.

Table VII and Figure 15 record the effects on alkali cellulose autoxidation of a series of typical antioxidants added to the steeping solution in 0.1% con-

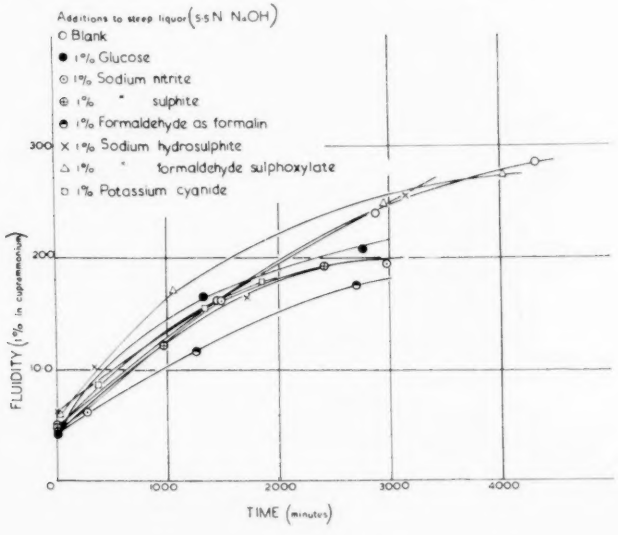

Additions to steep liquor (5.5 N NaOH)
○ Blank
● 1% Glucose
⊙ 1% Sodium nitrite
⊕ 1% " sulphite
◓ 1% Formaldehyde as formalin
× 1% Sodium hydrosulphite
△ 1% " formaldehyde sulphoxylate
□ 1% Potassium cyanide
FLUIDITY (1% in cuprammonium)
TIME (minutes)

FIG. 14. *Effect of various oxidizable substances on autoxidation of alkali cellulose.*

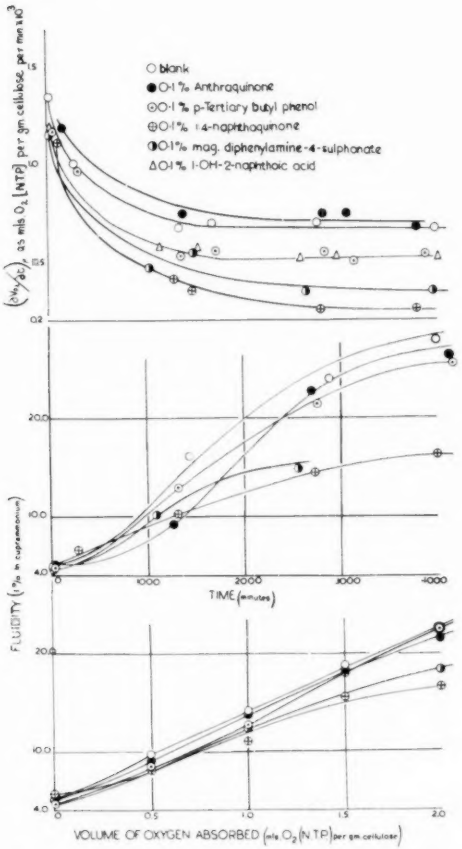

○ blank
● 0·1 % Anthraquinone
⊙ 0·1 % p-Tertiary butyl phenol
⊕ 0·1 % 1:4-naphthoquinone
◑ 0·1 % mag. diphenylamine-4-sulphonate
Δ 0·1 % 1-OH-2-naphthoic acid
TIME (minutes)
VOLUME OF OXYGEN ABSORBED (mls. O2 (N.T.P.) per gm. cellulose)

FIG. 15. *The effect of various antioxidants on autoxidation of alkali cellulose (at 25° C and $P_{O_2} = 700$ mm. Hg).*

centration. Of these, 1:4 naphthaquinone and the magnesium salt of diphenylamine-4-sulfonic acid showed pronounced antioxidant activity, depressing markedly both the rates of oxygen absorption and of fluidity rise. Anthraquinone, *p*-tertiary butyl phenol, and 1-hydroxy-2-naphthoic acid showed a much lower degree of activity. It is interesting to note that these antioxidants had no effect upon the initial rate of oxygen absorption, but affected only its subsequent course, indicating that they were functioning by inhibiting a radical chain reaction rather than influencing the chain-initiating process of aldehyde-group oxidation. Here again (Figure 15) antioxidant activity is accompanied by a fall in the amount of cellulose depolymerization resulting from a given absorption of oxygen.

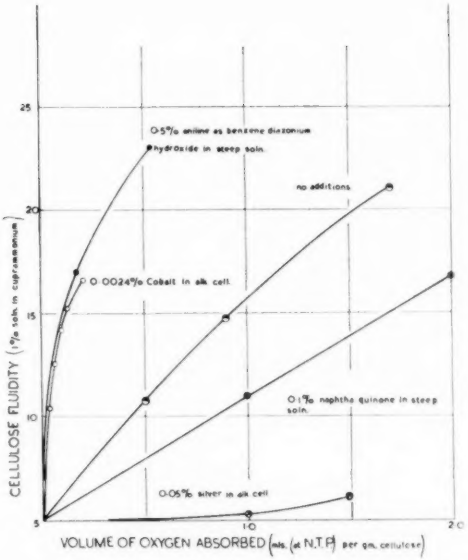

0·5% aniline as benzene diazonium hydroxide in steep soln.
no additions
0·0024% Cobalt in alk. cell.
0·1% naphtha quinone in steep soln.
0·05% silver in alk. cell
CELLULOSE FLUIDITY (1/% soln. in cuprammonium)
VOLUME OF OXYGEN ABSORBED (mls. (at N.T.P.) per gm. cellulose)

FIG. 16. *The effect of various catalysts and antioxidants on the depolymerization efficiency of alkali cellulose autoxidation.*

Discussion

The following general observations may be made from the various experimental results in the present paper, and from the published work quoted.

1. Catalysis of alkali cellulose autoxidation by the incorporation of "free radical"-generating materials increases the initial rate of oxygen absorption.

2. Catalysis by transition metals and inhibition by both silver and organic antioxidants do not affect the initial reaction rate but have a major effect upon subsequent stages of the reaction.

3. Positive catalysis, whether by free radicals or by transition metals, is accompanied by an increase in the amount of cellulose depolymerization resulting from a given absorption of oxygen, whereas negative catalysis by silver and by organic antioxidants reduces the ratio of depolymerization to oxygen absorption (see Figure 16). Indeed, Figure 16 shows hardly any rise of fluidity for an oxygen consumption of 1 ml. per g. cellulose when 0.05% silver is present.

TABLE VI. EFFECT OF VARIOUS OXIDIZABLE SUBSTANCES ON AUTOXIDATION OF ALKALI CELLULOSE (AT 25°C AND P_{O_2} = 700 MM. HG)

Composition of steep solution	Time (min.)	Velocity coefficient (ml. O_2/g. cell./min. (n.t.p.)$\times 10^3$)	Time (min.)	Fluidity (1% solution)
5.5*N* NaOH	34	1.34	0	5.0
	266	1.01	1,440	16.2
	1,337	0.69	2,880	23.9
	2,780	0.70	4,320	28.5
	4,268	0.64		
5.5*N* NaOH + 1% sodium nitrite	17	(1.04)	0	4.8
	232	0.97	280	6.1
	1,488	0.68	1,480	16.1
			2,980	19.4
5.5*N* NaOH + 1% sodium hydrosulfite	23	2.10	0	6.2
	337	1.49	353	10.2
	1,368	1.02	1,718	16.4
	2,764	0.86	3,153	25.5
5.5*N* NaOH + 1% glucose	22	5.1	0	4.2
	1,481	1.01	1,330	16.5
	3,082	0.72	2,770	20.7
5.5*N* NaOH + 1% sodium sulfite	22	1.27	0	4.5
	1,145	0.81	980	12.1
	2,745	0.60	2,420	19.2
5.5*N* NaOH + 1% potassium cyanide	35	1.28	5	5.3
	1,490	0.91	380	8.6
	2,815	0.54	1,340	15.5
			1,850	17.8
5.5*N* NaOH + 1% sodium formaldehyde sulfoxylate	44	4.9	30	5.9
	1,222	1.05	1,065	17.1
	2,954	0.89	2,955	24.8
	3,915	0.56	4,035	27.4
5.5*N* NaOH + 1% formaldehyde	26	0.84	0	4.6
	295	0.79	1,265	11.6
	1,405	0.32	2,705	17.4
5.5*N* NaOH + 1% phenol	—	—	0	5.0
	—	—	1,440	13.0
	—	—	2,880	20.0
	—	—	4,320	26.1
5.5*N* NaOH + 2% hydroquinone	—	—	0	5.0
	—	—	1,440	12.9
	—	—	2,880	16.1
	—	—	4,320	18.4

4. Reducing-group production, for a given oxygen absorption, is increased by positive catalysts and decreased by inhibitors.

These observations allow the general reaction scheme, already postulated, to be amplified.

Chain initiation occurs by the reaction of an alkali-sensitized, probably enolized reducing group in cellulose, with an oxygen molecule:

$$\text{CELL.—CHO(I)} + O_2 \longrightarrow \text{CELL.=CO—(II)} + \text{—HO}_2\text{(III)}; \quad \text{(i)}$$

and there follows a chain reaction in which unmodified anhydroglucose units adjacent to the radical (II) in the gel structure are oxidized:

$$\text{CELL.:CO—(II)} + O_2 \longrightarrow \text{CELL.:CO.OO—(IV)} \quad \text{(ii)}$$

TABLE VII. Effect of Various Antioxidants on the Autoxidation of Alkali Cellulose

Composition of steep solution	Time (min.)	Rate of oxygen absorption (ml. O_2 (n.t.p.) per g. cell./min. $\times 10^3$)	Time (min.)	Fluidity (1% solution)	Volume of oxygen absorbed (ml. O_2 (n.t.p.) per g. cell.)	Fluidity (1% solution)
5.5*N* NaOH	34	1.345	0	5.0	0.0	5.0
	266	1.01	1,440	16.2	0.5	9.6
	1,337	0.686	2,880	23.9	1.0	14.1
	1,699	0.700	4,320	28.5	1.5	18.7
	4,000	0.642			2.0	22.5
5.5*N* NaOH + 0.1% 1-hydroxy-2-naphthoic acid	35	1.19				
	1,165	0.57				
	1,545	0.57				
	2,607	0.51	—	—	—	—
	2,981	0.53				
	4,040	0.53				
5.5*N* NaOH + 0.1% naphthaquinone	112	1.12	275	6.3	0.0	5.4
	1,300	0.41	1,310	10.3	0.5	7.7
	1,478	0.35	2,725	14.5	1.0	10.9
	2,802	0.26	4,155	15.9	1.5	15.4
	3,800	0.27			2.0	16.6
5.5*N* NaOH + 0.1% anthraquinone	148	1.19	20	5.2	0.0	5.1
	1,393	0.75	1,260	9.2	0.5	7.7
	2,843	0.74	2,700	22.8	1.0	13.4
	3,079	0.74	4,130	26.6	1.5	18.1
	3,800	0.63			2.0	21.5
5.5*N* NaOH + 0.1% *p*-tertiary butyl phenol	55	1.17	30	4.8	0.0	4.7
	318	0.97	1,325	13.0	0.5	8.2
	1,385	0.53	2,765	21.5	1.0	12.7
	1,729	0.55	4,195	25.5	1.5	17.8
	2,831	0.54			2.0	22.4
	3,153	0.50				
	4,000	0.53				
5.5*N* NaOH + 0.1% magnesium diphenylamine-4-sulfonate	20	1.17				
	1,041	0.47	0	4.6	0.0	4.6
	1,484	0.55	1,079	10.1	0.5	7.9
	634	0.35	2,544	14.9	1.0	12.2
	3,957	0.35			2.0	18.2

$$\text{CELL..CO.OO—(IV)} + \text{CELL..H(V)} \longrightarrow \text{CELL..CO.OOH(VI)} + \text{CELL.—(VII)} \quad \text{(iii)}$$

$$\text{CELL.—(VII)} + O_2 \longrightarrow \text{CELL.—OO—(VIII)} \quad \text{(iv)}$$

$$\text{CELL..OO—(VIII)} + \text{CELL..H(V)} \longrightarrow \text{CELL..OOH(IX)} + \text{CELL.—(VII)}. \quad \text{(v)}$$

A chain reaction involving oxygen absorption will then result by alternation of processes (iv) and (v).

The hydroperoxides (VI) and (IX) are likely to hydrolyze rapidly in alkaline solution; *e.g.*,

$$\text{CELL..OOH(IX)} + H_2O \longrightarrow \text{CELL..OH(X)} + H_2O_2. \quad \text{(vi)}$$

Here (X) will lose water if the OH is attached to C_2, C_3, or C_6, giving an aldehydic or ketonic cellulose. If the OH is attached to C_4 or C_5, the structure of (X) will resemble that of a hemiacetal and undergo rapid hydrolysis with consequent scission of the cellulose molecule at that point and the development of reducing properties. If the OH is attached to C_1, the structure will be that of an acid orthocarboxylic ester and will hydrolyze rapidly, again with scission of the cellulose molecule.

The hydroperoxide (IX) may undergo thermal fission, resulting in chain branching:

$$\text{CELL..OOH} \longrightarrow \text{CELL..O—(XI)} + \text{—OH(XII)}. \quad \text{(vii)}$$

In the presence of a catalytically active metal, this process will be accelerated:

$$CELL.OOH + M^{++} \longrightarrow CELL.O\ + {-}OH + M^{+++} \quad \text{(viii)}$$

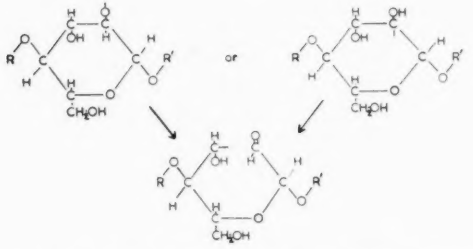
at the expense of reaction (vi).

It seems likely, therefore, that the free-radical chain character of the reaction will be emphasized in the presence of catalytically active metals where the equilibrium peroxide concentration is low, and that in their absence some oxidation by hydrogen peroxide will take place.

The evidence is that in the presence of these metals and of added free radicals the over-all course of oxidation is diverted in the direction of increased cellulose depolymerization. It is reasonable to suppose that radical dehydrogenation of cellulose occurs specifically at sites where molecular scission, either directly or upon subsequent addition of oxygen, can occur. Oxidation by hydrogen peroxide, on the other hand, may be considered to be a more random process capable of attacking the anhydroglucose unit without necessarily resulting in depolymerization. In this respect it is interesting to note that Walsh [20] and others find a tendency for the hydrocarbon radical $R.CH_2O-$ to break down:

$$R.CH_2O- \longrightarrow R- + CH_2O \quad \text{(formaldehyde)}$$

and it seems possible that a dehydrogenated anhydroglucose unit might undergo a similar reaction:



Thus, an alkali-labile link in the cellulose molecule might be produced without the addition of oxygen at this point being essential to the degradation process.

It is quite evident at this stage that, given a free-radical-propagated autoxidation chain reaction, the possible processes leading to cellulose depolymerization are exceedingly numerous, and a great deal more research to determine the character of the structure of the modified residual cellulose and of the soluble fragments is required. The present paper and its predecessor have served their purpose if they have indicated that serious consideration must be given to the concept of alkali cellulose autoxidation as a process involving free radicals and to the necessity for reviewing other autoxidation reactions of cellulose in a similar light.

Acknowledgment

The authors wish to thank Messrs. E. W. Courts and R. Ellis for experimental assistance, Dr. R. M. Lodge for helpful discussion, and the Directors of Courtaulds, Limited, for permission to publish.

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(Manuscript received May 9, 1949.)

Cellulose Studies*

XI. Acetal Type of Methoxyl Groups in Methanolyzed Celluloses

P. C. Mehta and Eugene Pacsu

Contribution from the Textile Foundation and the Frick Chemical Laboratory, Princeton University

Abstract

Native cotton and commercial viscose rayon were degraded by using a saturated solution of hydrogen chloride (about 43%) in methanol at 0° C. It was found that, on the average, 8.1 bonds in native cotton suffered methanolysis during the first 6 hrs. of the reaction, whereas in the ensuing period of 666 hrs. only 1.6 bonds became cleaved. The results indicate that the initial reaction comes to a practical standstill after about the same stage of degradation has been reached as in the mild hydrolytic scission of the same materials (D.P. ~ 250 for cotton, and D.P. ~ 60 for viscose rayon).

In order to gain information as to the nature of the methoxyl groups in the methanolyzed products, a study of the rate of hydrolysis of the latter was made. Evidently, if the classical concept of cellulose structure is correct—that is, if only normal methyl glucopyranoside end-groups are present—then the rate of acid hydrolysis, as measured by the increase in the reducing power, should be of the order of magnitude shown by the normal methyl glucopyranosides. On the other hand, a very fast rate of hydrolysis, which is characteristic for the open-chain dimethyl acetals of the sugars, would constitute evidence for the presence of such types of residues; hence, it would favor the new concept of cellulose structure.

The results showed that more than one-half of the material in the case of viscose rayon and about one-half in that of native cotton were hydrolyzed by 0.05*N* HCl at 60°C in a period of 48 hrs., which is shorter beyond all comparison than the half-life (3,450 hrs.) of methyl α-glucopyranoside under identical conditions. These results are considered to supply the chemical proof for the presence of the acid-sensitive, open-chain glucose residues which were suggested in the new formula for cellulose.

IN AN EARLIER PAPER [7] were described the results of a heterogeneous hydrolysis of cellulose in dilute solutions of organic acids. In later experiments, cellulose was degraded under more drastic conditions, using a saturated solution of hydrogen chloride (about 43%) in methanol at 0°C. Native cotton and commercial viscose rayon were employed as two typical cellulosic materials.

Native cotton was first purified by the following series of processes: (1) extraction with acetone for 10 hrs. under reflux, followed by drying overnight in air; (2) extraction with benzene for 10 hrs. under reflux, followed by drying overnight in air; (3) boiling with 2% sodium hydroxide solution under nitrogen for 18 hrs.; (4) washing in hot tap water three times, and immersing in tap water for 18 hrs.; (5) washing in distilled water (8 portions) and finally with methanol (3 portions); (6) drying overnight in an oven at 50°C.

The viscose rayon was desized by washing in hot soap solution at about 70°C for 2 hrs.

A methanolic solution of hydrogen chloride was prepared by passing the gas from a tank through a wash bottle containing concentrated sulfuric acid and through a trap into a flask containing methanol. The latter was cooled to between 0°C and −5°C by immersion of the flask in a bath of ice and salt. It took approximately 1 day to saturate 1 l. of methanol with hydrogen chloride. At the end of that period, the solution was analyzed for its hydrogen chloride content by diluting 1 ml. of the solution to 100 ml. and titrating 10 ml. of the diluted solution with 0.1*N* sodium hydroxide solution.

* The first paper in this series appeared in the October, 1945, issue of TEXTILE RESEARCH JOURNAL. Papers II–VIII were published in March, April, June, July, August, October, and November, 1946. Paper IX appeared in the August, 1947, issue, and X in July, 1948.

TABLE I. DEGREES OF POLYMERIZATION OF NATIVE COTTON AND VISCOSE RAYON METHANOLYZED AT 0°C WITH 43% HYDROGEN CHLORIDE IN METHANOL

Sample	Hrs. of methanolysis	$[\eta]$*	D.P. $(260\times[\eta])$	No. of cleaved bonds†
Native cotton	0	9.60	2,500	0
Native cotton	6	1.05	275	8.1
Native cotton	24	0.99	257	8.7
Native cotton	672	0.90	234	9.7
Viscose rayon	0	1.40	364	—
Viscose rayon	168	0.30	78	—

* $[\eta]$ denotes $\left[\frac{\eta_{sp}}{C}\right]_{C\to 0}$; C equals g. per 100 ml.

† No. of cleaved bonds $= \frac{\text{D.P. cell. native}}{\text{D.P. cell. degr.}} - 1.$

About 5-g. samples of the purified cellulosic material, native cotton or viscose rayon, were powdered in a Wiley mill, dried overnight in an oven at 50°C, and then steeped in about 200 ml. of the reagent in a series of glass-stoppered Erlenmeyer flasks. The latter were immersed in an ice bath and left in a refrigerator, thus maintaining the temperature at 0°C for long periods of time. At the end of the desired intervals the samples were filtered by suction through sintered glass and washed with methanol until all the acid was removed. The samples were then washed with water, finally with acetone, and dried overnight in an oven at 50°C. The filtrate and first (methanol) washing were preserved.

The hydrogen chloride content was checked at the end of the reaction period, and no significant loss was detected even at the end of 28 days.

The degrees of polymerization of the various products were determined by measuring the cuprammonium viscosities as described previously [7]. The results are summarized in Table I.

The filtrate and the first washing from each experiment were united and distilled under reduced pressure, the residue was washed several times with methanol, and the distillation was continued until no odor of hydrogen chloride was detected. The sirupy residue was dried under reduced pressure over solid sodium hydroxide for several days; in most cases, only negligible amounts (less than 2% from cotton after 672 hrs. of reaction time) of a pale brown, sirupy material of unknown composition were obtained.

The results of these experiments strongly support the previously expressed view that native cellulose contains acid-sensitive bonds which are responsible for its rapid initial degradation in acidic media. The figures in the last column of Table I reveal the interesting fact that, on the average, 8.1 bonds in native cellulose suffer methanolysis during the first 6 hrs. of the reaction, whereas in the ensuing period of 666 hrs. only 1.6 bonds become cleaved. Considering the unusually high acid concentration of the reagent, it is remarkable that the initial reaction comes to a practical standstill after about the same stage of degradation has been reached as in the mild hydrolytic scission of the same materials (D.P. – 250 for cotton, and D.P. – 60 for viscose rayon).

Once again, the experimental results suggest that the simple linear formula of cellulose with its "uniform and equivalent, covalent glycosidic linkages" is inadequate to explain the behavior of cellulose upon acid hydrolysis or methanolysis.

It is also evident that the view according to which the reaction stops after the 1,4-glycosidic bonds in the *amorphous* region of the fiber have been cleaved is untenable. This conclusion follows from the fact that the reaction abruptly comes almost to an end *without any appreciable loss of material*. Therefore, during this important first phase of degradation only about 3 out of 1,000 cleavable bonds are affected, whereas the other 997 bonds, now belonging to the shortened and comparatively acid-resistant molecules with an average value of D.P. – 250, remain practically intact. In the light of the definition the "accessible region," in this case, becomes identical with the 0.3% extremely acid-sensitive bonds. However, the order of accessibility found by different methods is of an entirely different magnitude from this insignificant percentage of bonds broken during the long period of acid interaction. Thus, Mark and coworkers [4] found that cellulose reacts very rapidly with heavy water and concluded that the extent of

the reaction is a measure of the accessibility of the cellulose sample. From the accessibility they estimated the amount of amorphous region present in the sample studied to be 21% for cotton and 66% for rayon. These figures are in fairly good agreement with Hermans' [6] estimates obtained from density measurements.

On the other hand, it is almost certain that the very first attack of an acidic reagent is confined to the acid-sensitive bonds occurring in the *accessible* region of the fiber. Therefore, the acid-sensitive bonds occurring in the inaccessible regions of the resulting hydrocelluloses would mostly remain intact and unreactive. Because of the more amorphous nature of regenerated native cellulose or of viscose rayon, it is to be expected that the "limit hydrocelluloses" from these materials should show a much lower D.P. value than those obtainable from native cellulose, or from artificial fibers with higher crystallinity such as tire-cord rayon or Fortisan. This, indeed, appears to be the case. The D.P. values for the "limit hydrocelluloses" from native cotton, regenerated celluloses, and tire-cord rayon have been found to be -250, -60, and -120, respectively.

Since we have not yet been able to obtain from any cellulosic source a primary degradation product with a lower average D.P. than -60, the value of $2^6 = 64$ has been chosen as the probable value of the degree of polymerization of a "limit hydrocellulose chain molecule," which is supposed to be devoid of acid-sensitive linkages and which is regarded as the building unit of the cellulose fiber [9].

Methanolic hydrogen chloride under our experimental conditions presumably attacks the acid-sensitive linkages only. If so, then investigation as to the nature of the methoxyl groups present in the degradation products should yield valuable information concerning the type of bonds from which such methoxyl groups originate and, hence, concerning the structure of cellulose. In the following section it will be shown that our experimental results revealed the occurrence of true acetal-type bonds in cellulose.

Nature of the Methoxyl Groups Present in Methanolyzed Celluloses

In order to get some insight into the reaction of methanolysis it was necessary to know whether each new reducing group formed by a scission of the chain was blocked by a methoxyl group and, if so, to examine the nature of this methoxyl—whether it was a simple glycosidic methoxyl, in accordance with the well-known linear formula of cellulose, or was of the open-chain acetal-type, as required by the suggested [9] new formula for cellulose (Formula I).

TABLE II. COPPER NUMBERS OF HYDROLYZED AND METHANOLYZED CELLULOSES

Substance	Weight	Ml. of 0.0416 N $KMnO_4$	Copper numbers (ml. of 0.0416 N $KMnO_4$ per g. material)
Native cotton			
1	1.0064	0.15	0.15
2	1.0130	0.19	0.18
Hydrocellulose (D.P. ~260) from native cotton			
1	1.0080	10.50	10.42
2	0.9996	10.40	10.40
Native cotton methanolyzed at 0°C for 168 hrs. (D.P. ~260)			
1	1.0092	0.95	0.94
2	1.0018	0.99	0.99
Hydrocellulose (D.P. ~65) from viscose rayon			
1	1.0207	23.25	22.78
Viscose rayon methanolyzed at 0°C for 168 hrs. (D.P. ~70)			
1	1.0099	11.84	11.72
2	0.9987	12.23	12.25

First, native cotton which was methanolyzed at 0°C for 25 days with 4% hydrogen chloride in methanol was examined for its methoxyl content by the Vieböck and Schwappach semimicro method [13] as modified by Clark [2]. The results of three estimations on the same material indicated a methoxyl content of 0.21%, 0.18%, and 0.19%, respectively. However, reflection shows that it is not possible by this method to measure the methoxyl content with any degree of accuracy, since if there is 1 methoxyl group at the end of every chain of 250 glucose-anhydride units, the methoxyl content would not exceed 0.1%, which is less than the experimental error involved in this determination.

A more sensitive method would be to compare the reducing powers of the methanolyzed celluloses with those of the hydrocelluloses of about the same degree of polymerization. The former should show markedly lower reducing powers than the latter, and if all the reducing end-groups formed by the scission of the chains were blocked by methoxyl groups, the

methanolyzed products should have no reducing capacity at all.

We first used the hypoiodite method of end-group estimation at pH 9.2 and pH 10.6, but could not get reproducible results on the same samples. This was not entirely unexpected in view of our earlier experience [11] with this particular method when applied to cellulosic materials with a high degree of polymerization.

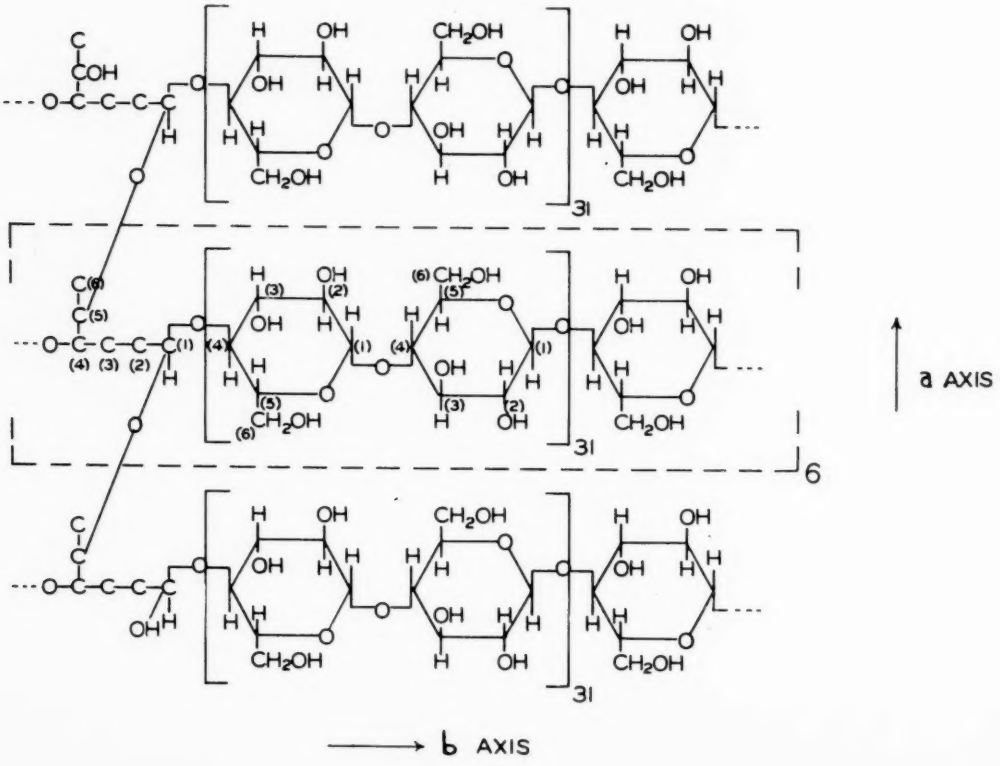
We then followed the older "copper number" method of Braidy [1], as developed by Clibbens and Geake [3], which gave satisfactory results. The only deviation from the original procedure was that approximately 1-g. samples and 50 ml. of the sodium carbonate-sodium bicarbonate-copper sulfate solution were used instead of the 2.5-g. samples and 100 ml. of the solution as recommended by Braidy. The results of the determinations are summarized in Table II.

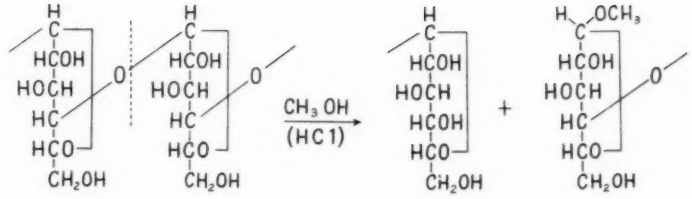
Purified native cotton shows a very low copper number, and our values compare well with the results of other investigators [3]. Also, the hydrocelluloses from native cotton and viscose rayon show much higher reducing power than the corresponding methanolyzed products, as would be expected. The only unexpected result is that methanolyzed viscose rayon has a relatively high copper number, indicating that there are some free reducing groups present. It is not impossible, however, that the latter are the result of a partial hydrolysis of the methyl derivatives during the working-up process.

Regarding the nature of the methoxyl groups in the methanolyzed products, it is obvious that a cellulose chain molecule with "uniform and equivalent, covalent glycosidic linkages" should give rise to shorter chains with a normal, methyl glucopyranoside residue at one end of a chain (Reaction Scheme 1).

On the other hand, the suggested [9] new struc-

Formula I





Reaction Scheme I

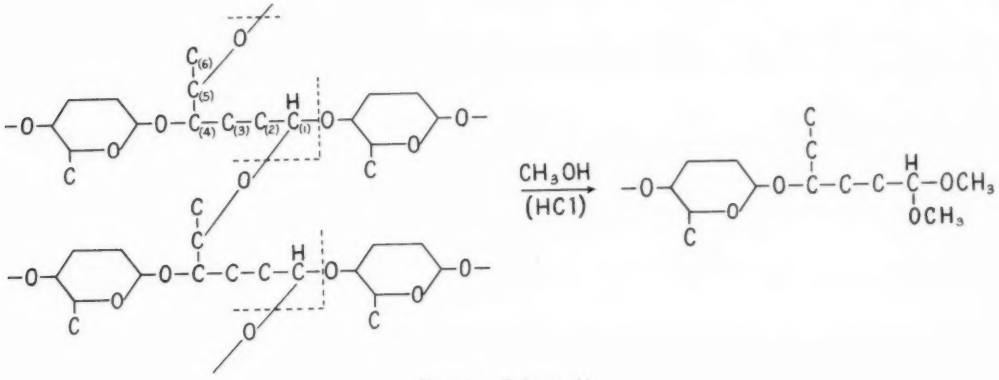
ture of cellulose (Formula I) would require the formation of true dimethylacetals from the open-chain glycose-anhydride units (Reaction Scheme II).

Evidently, a study of the *rate* of hydrolysis of the methoxyl-containing degradation products should provide a good test as to the true structure of the cellulose molecule. If the classical concept of cellulose structure is correct—that is, if only normal methyl glucopyranoside end-groups are present—then the rate of acid hydrolysis, as measured by the increase in the reducing power, should be of the order of magnitude shown by the normal methyl glucopyranosides. On the other hand, a very fast rate of hydrolysis, which is characteristic for the open-chain dimethyl acetals of the sugars [5, 10, 12], would constitute evidence for the presence of residues of this type; hence, it would favor the new concept of cellulose structure.

For these experiments, fresh samples of the same materials—methanolyzed native cotton and viscose rayon—were hydrolyzed with 1*N* hydrochloric acid at 60° C for 72 hrs., and their copper numbers were determined after washing and drying of the products (Table III). The hydrolysis was practically complete and the copper numbers had reached about the same values as those shown by the corresponding hydrocelluloses, thus indicating a very rapid reaction.

Referring to the literature, it was found that the $k_1 aH^+$ value for the hydrolysis of methyl α-glucopyranoside is 3.81×10^{-3} (log; min.) (using 1*N* hydrochloric acid at 60° C) [8]. Since the half-time of hydrolysis is about 132 hrs., the time required for complete hydrolysis should be approximately 1,300 hrs., which is of an entirely different order of magnitude from the time (72 hrs.) used for the hydrolysis of the methanolyzed celluloses, in spite of the fact that the hydrolysis in the latter case is heterogeneous and would therefore be expected to be slower if the same bond were being hydrolyzed in the two cases.

In order to make a direct comparison of the rates of hydrolysis possible, methanolyzed viscose rayon (D.P. – 70) and methanolyzed native cotton (D.P. – 260) were hydrolyzed under the same conditions as those given by Moelwyn-Hughes [8] (0.05*N* hydrochloric acid at 60° C). The half-time of hydrolysis of methyl α-glucopyranoside under these conditions



Reaction Scheme II

TABLE III. COPPER NUMBERS AFTER HYDROLYSIS OF METHANOLYZED CELLULOSES

Substance	Weight	Ml. of 0.0416 N $KMnO_4$	Copper numbers (ml. of 0.0416 N $KMnO_4$ per g. material)
After hydrolysis with 1N HCl at 60°C for 72 hrs.:			
Methanolyzed native cotton (D.P. ~260)	1.0068	10.85	10.78
Methanolyzed viscose rayon (D.P. ~70)	1.0146	24.85	24.50
After hydrolysis with 0.05N HCl at 60°C for 48 hrs.:			
Methanolyzed native cotton (D.P. ~260)	0.9937	4.83	4.86
Methanolyzed viscose rayon (D.P. ~70)	0.4300	9.05	21.05

is 3,450 hrs. [5*a*]. After 48 hrs. the samples were filtered, washed, and dried, and their copper numbers were determined (Table III).

The results show that more than one-half of the material in the case of viscose rayon and about one-half in that of native cotton is hydrolyzed in a period of 48 hrs., which is shorter beyond all comparison than the half-life (3,450 hrs.) of methyl α-glucopyranoside. It is known that the copper-number method is not stoichiometric and requires more or less identical conditions for a fair comparison. However, according to the data of Clibbens and Geake [3] the difference in the copper numbers of the same materials, using 1-g. and 2.5-g. samples, is not considerable. Since our results are so outstandingly different from those which would be expected for a methyl glucopyranoside, we feel justified in overlooking this error of 5% to 10% due to the difference in weights of the samples used for the determinations.

It is quite evident from these results that in the methanolysis of cellulose under our experimental conditions, the methoxyl groups introduced into the molecule are not normal glucosidic methoxyls, as required by the single-chain formula of cellulose, but are much more labile and must be of the open-chain acetal type. We consider that these results supply the chemical proof for the presence of open-chain glucose residues which were suggested in the new formula for cellulose (Formula I).

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(*Manuscript received June 27, 1949.*)

Letters to the Editor

Dynamic Properties of Polymeric Materials

The Textile Foundation
and Frick Chemical Laboratory,
Princeton University
Princeton, New Jersey

August 12, 1949

To the Editor
Textile Research Journal
Dear Sir:

Considerable interest is attached to the problem of the mechanical properties (dynamic modulus G_{dyn} and dynamic viscosity η_{dyn}) of high polymers subjected to harmonic vibrations of varying frequencies. In particular, it has been observed that η_{dyn^ω} is relatively independent of frequency ($\omega/2\pi$) over a considerable frequency range [4, 5, 6, 8]. The question has also arisen as to whether or not a relationship exists between the dynamic energy losses and static phenomena such as creep.

Kuhn has shown how, for a material for which the creep curve is linear with logarithmic time, one may predict the dynamic energy losses in free vibration experiments [7]. In the course of his theoretical arguments he described the mechanical system approximately in terms of a distribution of relaxation times, which is a rectangular function on a logarithmic plot—namely,

$$\begin{aligned} G(\tau)d(\log \tau) &= G_a \qquad a < \tau < b \\ &= 0 \qquad a > \tau,\ \tau > b \end{aligned} \tag{1}$$

This distribution of relaxation times had previously been extensively investigated by Becker for ferromagnetic hysteretic behavior [2, 3]. The same function was also shown to fit stress relaxation data for polyisobutylene [1].

By use of the distribution function (1), the correlation between stress relaxation and dynamic properties is exact and remarkably simple, and is mathematically even more direct than the correlation between creep data and dynamic properties. If stress relaxation is linear when plotted against logarithmic time, the data can be expressed in terms of the distribution function (1), where a and b are, respectively, smaller than and greater than the smallest and largest recorded times. For dynamic experiments in which $1/b \ll \omega \ll 1/a$, the following very simple relationship exists:

$$\eta_{dyn}\omega = \frac{\pi}{2\epsilon_a \log_e 10} \begin{pmatrix}\text{slope of relaxation curve} \\ \text{plotted } vs. \log_{10} \text{time}\end{pmatrix}, \tag{2}$$

where ϵ_a is the fixed strain at which the stress relaxation measurement is being carried out.

This relationship was applied to stress relaxation data [9] for rubbers, and the predicted values of η_{dyn^ω} were compared with observed values of η_{dyn^ω} for the same rubber stocks [4]. Also, experimental data were obtained for stress relaxation and dynamic properties of various textile fibers, and comparison between η_{dyn^ω} values predicted from equation (2) and observed values was made. These comparisons are shown in Table I. It is clear from this table that an order-of-magnitude agreement exists between the observed and the calculated values. In

TABLE I.

Material	Temp. (°C)	Calculated $\eta_{dyn\omega}$ (dynes/cm.²)	Observed $\eta_{dyn\omega}$ (dynes/cm.²)
Hevea gum stock	40°	0.026×10^6	0.24×10^6
	100°	0.045	0.13
Hevea tread stock	40°	0.48	2.5
	100°	0.55	1.1
GR-S gum stock	40°	0.11	0.85
	100°	0.11	0.42
GR-S tread stock	40°	1.1	7.8
	100°	0.40	3.0
Butaprene gum	40°	0.17	1.7
	100°	0.25	0.70
Butaprene tread	40°	0.42	4.1
	100°	0.40	1.5
Neoprene gum	40°	0.33	0.85
	100°	0.33	0.68
Neoprene tread	40°	0.82	3.9
	100°	0.86	2.0
Nylon	20°	0.8×10^9	3.8×10^9
Viscose rayon	20°	1.4×10^9	4.8×10^9
Acetate rayon	20°	1.2×10^9	1.5×10^9
Feather keratin	20°	0.70×10^9	1.5×10^9
Raw silk	20°	2.3×10^9	3.8×10^9
Polyethylene	20°	0.18×10^9	0.82×10^9

most cases the losses predicted from stress relaxation data are less than the observed dynamic losses. Papers detailing the theoretical and experimental developments will appear soon in TEXTILE RESEARCH JOURNAL.

Acknowledgment

Grateful acknowledgment is made to the Office of Naval Research, which supported this work through Contract No. N7-onr-374, Task Order I.

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Correction

In the article "Evaluation of Roll Wool Felts for Arctic Footwear," by Thora M. Plitt Hardy, which appeared in the July, 1949, issue, pages 427–435, the specimen measurements given as "2-sq.-in." on pages 427, 432, and 433 should have been "2 in. square."

INDUSTRIAL SECTION

A Dynamically Balanced Fatigue Tester for Rayon Tire Cord*

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ONE OF THE RECOGNIZED desirable characteristics of a cord for making tires is the ability to withstand long periods of flexing in a tire without fatigue failure. In order to test rapidly and economically large numbers of experimental cords it is necessary to have simple and rapid fatigue tests, the results of which can be either correlated with or interpreted in terms of the ratings of the same cords in tires. Various mechanical devices have been described for measuring the fatigue resistance of tire cords without making tires of them. One of these testers cyclically deforms cord which has been imbedded in rubber [4]. This imbedding in rubber simulates the conditions in a tire, but so much work is required in applying adhesive and rubber to rayon cords for this test that it is unsuitable for testing large numbers of samples. Another class of testers cyclically stretches and relaxes cords until they fail under the peak applied load. One tester of this latter class maintains a selected minimum tension by taking up the slack during the relaxation part of each cycle by a ratchet mechanism [2]. This method is satisfactory if the frictional effects of the take-up mechanism are reproducible. Another tester of this latter class applies the load by hanging a weight on the lower end of a cord while the upper end is oscillated up and down [1]. The high temperature required with this tester to get a reasonably short life causes considerable chemical degradation [5]. If the life is shortened by increasing the stroke instead of raising the temperature, the weights vibrate excessively. To overcome this latter difficulty the tester described herein was designed so that the forces acting on the weights were very nearly balanced throughout the stretching and relaxing cycle. This permits a con-

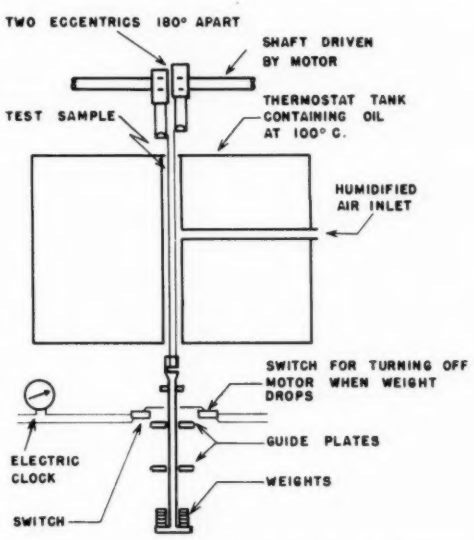

FIG. 1. *Schematic diagram of dynamically balanced fatigue tester for rayon tire cord.*

* Presented by W. E. Roseveare at the Clemson, South Carolina, meeting of the Fiber Society, April 15, 1949.

† Present address: Goodyear Tire and Rubber Co., Akron, Ohio.

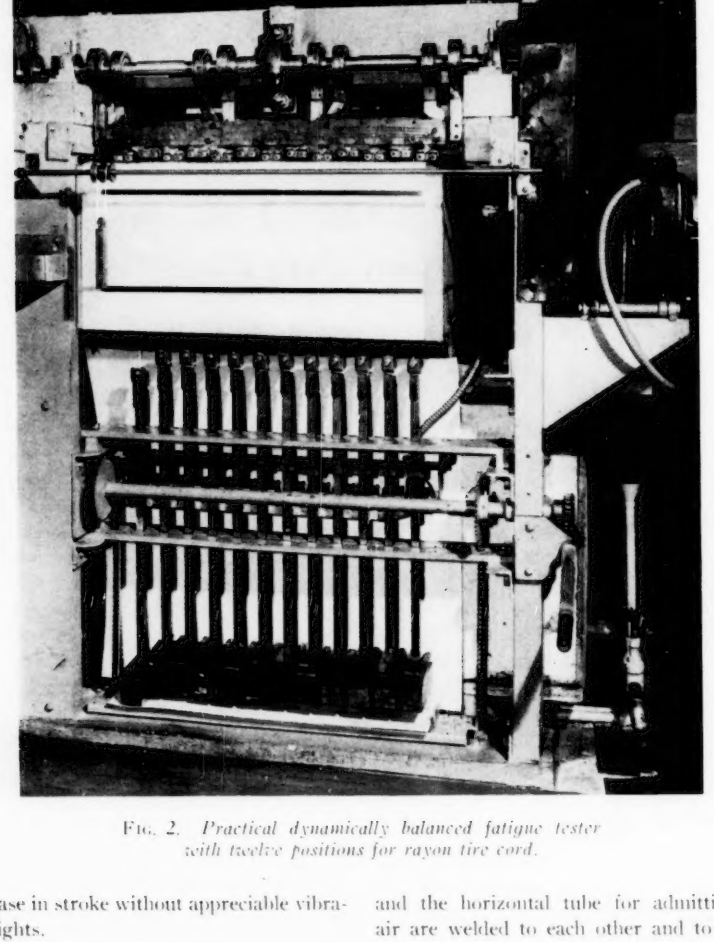

FIG. 2. *Practical dynamically balanced fatigue tester with twelve positions for rayon tire cord.*

siderable increase in stroke without appreciable vibration of the weights.

Description of Tester and Mechanical Principles

A schematic drawing of the dynamically balanced fatigue tester is shown in Figure 1. A weight is hung by equal lengths of the tire cord being tested from two eccentrics on the same shaft and out of phase by 180° so that during any fraction of the cycle of rotation of the shaft the lengthening of one cord is equal to the shortening of the other cord.

The thermostat tank shown in the figure surrounds nearly the whole length of the cord between the gripping jaws. The vertical tube surrounding the sample and the horizontal tube for admitting conditioned air are welded to each other and to the thermostat tank. This tank contains oil which is stirred and controlled thermostatically at 100 ± 1° C. The two switches below the thermostat tank are located so that the collar on the rod supporting the weight will open the switches when the cord breaks and the weight falls. One switch turns off the timing clock and the other turns off the motor which rotates the shaft.

A picture of a practical fatigue tester with twelve positions is shown in Figure 2. In this machine, the tubes surrounding the samples are 12 inches long and $^{7}/_{16}$ inch in diameter and have their upper ends constricted to $^{5}/_{16}$ inch to prevent excessive up-

ward flow of the hot air in the tubes. The upper jaws are mounted on either one or the other of two parallel plates, which are oscillated up and down 0.242 ± 0.002 inch by eccentrics attached near their ends. The lower jaws are attached to square rods having plates on the bottom for supporting U-shaped loading weights. These square rods pass through two plates with square holes, which prevent the rods from twisting or moving laterally but permit free vertical movement. Each of the upper and lower jaws has a cylindrical snubbing surface of 140° with a radius of curvature of $\frac{3}{8}$ inch and a clamp which grips the cords close to the cylindrical surface. This cylindrical snubbing surface is covered with a piece of "Hydroil" gasket liner No. 91305 to reduce the number of jaw breaks and the wearing of the snubbing surface. The gasket lining material is changed when it shows appreciable wear. Ordinary clamping jaws of the binding-post type were tried first, but they gave an excessive number of jaw breaks. The sample length of 16.75 inches includes the snubbed portions of the cords. The crank shown in the lower right portion of the photograph raises an elevator under all the weights to facilitate stringing up of samples and to permit simultaneous loading of all positions when the test is started. The switches for turning off the motor are wired in parallel so that the machine is stopped when the last weight falls. Each position has its own electric clock for automatically measuring the time for cord failure.

Auxiliary equipment not shown in the picture includes a bubble tank for saturating air with water at 42° C and automatic temperature controls for it and the thermostat tank. The tube carrying the air from the bubble tank to the high-temperature thermostat is heated to 42° C or higher to prevent condensation. At 100° C the relative humidity of the air surrounding the sample is 8% and the moisture content of rayon cords is maintained at a constant value of about 2%.

A summary of the conditions defining the fatigue test are given in Table I.

TABLE I. CONDITIONS DEFINING FATIGUE TEST

Sample length	16.75 in.
Stroke	1.44%
Frequency	3,000 c.p.m.
Load	1 g./den., 0.35 breaking tension or 0.175 breaking tension
Temperature	100°C
Relative humidity at 100°C	8%

Experimental Procedure

A 35-inch length of each sample of cord to be tested is tied in a loop to prevent change in twist. The loop is pulled over the rod on the front of the machine, down through the tester with a wire hook, and then attached to the lower clamps. During this operation sufficient tension is applied by hand to prevent twisting of the cords. An 8-ounce weight is hung on the upper end of the loop, as shown in the extreme left-hand position in Figure 2. After all positions have been strung up in the above manner, the elevator platform is raised so that as much as possible of the lower portions of the cords are in the thermostat. The air flow from the bubble tank is turned on and the flow is adjusted until a small amount of humidified air comes out the bottom of the thermostat, as detected by the condensation of moisture when a metallic surface is placed near the bottom of the tubes. After conditioning for 30 minutes, the cords are passed over the upper snubbers and clamped with the weights tensioning the cord. The portion of each cord loop in front of the upper jaws is cut away. The platform supporting the weights is lowered and the motor and clocks are started. After the last sample breaks, the fatigue lives are read from the electric clocks

An excessive number of jaw breaks were experienced until it was found that this could be prevented by coating the portions of the cord which were to be in the clamps of the tester with a dope made up by mixing 50 g. cellulose acetate flake, 30 g. dibutyl phthalate, 0.25 g. Sudan red oil, and 500 cc. of acetone. This dope was allowed to dry before the samples were placed in the tester.

Results Obtained with Tester

The stretching of one cord is equal to the contraction of the other cord in all periods of the cycle caused by rotation of the shaft. Therefore, the force acting on the weights should be constant throughout the cycle provided the relationship between the load and the elongation is linear and reversible. This condition is so well approximated with rayon cords up to 1.6% stroke that movement of the weights can scarcely be observed at any speed from 1 to 3,000 c.p.m. Even when the tester is operated near the natural vibration frequency of the cord-weight system there is no appreciable vibration of the weight.

This tester has been useful with the test conditions of Table I and a load of 1 gram per denier in

TABLE II. PROPERTIES OF RAYON AND COTTON CORDS

Type	Twist	Denier	Tenacity, g./den. Conditioned	Tenacity, g./den. Dry	% Elongation Conditioned	% Elongation Dry
Cotton X/4/2	14.2Z/17.1Z/10.5S	3,809	1.9	1.6	7.7 (10-lb. load)	5.1 (10-lb.load)
Rayon 1650/2	11.0Z/11.0S	3,690	2.84	3.37	10.1 (15-lb. load)	5.2 (15-lb.load)

showing up differences in the fatigue resistance of various types of rayon in cords which had the same structure and nearly the same strength and elongation under a load of 15 pounds. Under these conditions the fatigue lives of most commercial rayon tire cords are between 50 and 120 minutes. The coefficient of variation was found to be 25% for one sample of rayon tire cord. In most cases the average of six values is used as the fatigue rating, but a larger number of tests are required in comparing cords with small differences in fatigue resistance. These conditions are approximately those reported by the authors [5] as giving the fatigue lives of rayon cords nearly independent of creep and heat degradation. The changes in life produced by varying frequency, temperature, and moisture content were reported also. The logarithm of fatigue life was found to be a linear function of the load for two rayon cords, but the relative rating of the cords varied with the load. In order to obtain a better understanding of the use of this tester for cords of widely different character, the lives of the cords listed in Table II were measured with loads of 1 gram per denier and at 35% and 17.5% of their conditioned breaking tensions. The results of these measurements are given in Table III.

TABLE III. FATIGUE LIVES IN KILOCYCLES AT VARIOUS LOADS

	Kc. at 1 g./den.	Kc. at 35% conditioned breaking tension	Kc. at 17.5% conditioned breaking tension	Col. 3 / Col. 2
Undipped cords				
Cotton	below 0.1	51	3,000	59
Rayon	265	265	1,700	6.4
Cotton/rayon	.0004	0.19	1.8	
Dipped cords				
Cotton		84	4,500	54
Rayon		410	2,600	6.3
Cotton/rayon		0.20	1.7	

At 1 gram per denier the life of the cotton cord is less than 0.0004 of that of the rayon cord, but at loads of 35% of the breaking tension of the cord this ratio is 0.19. This latter type of loading places a relatively smaller load on the cotton, thereby increasing its life. Reducing the load from 35% to 17.5% of the breaking load increases still further the life of cotton relative to that of rayon. A comparison of the data in Table III shows that dipping the cords in a resorcinol-formaldehyde-latex adhesive [3] and drying has practically no effect on the relative lives, although the absolute values were increased by the dipping treatment.

The data of Table III are plotted in Figure 3 with logarithm of fatigue life as ordinate and tester load as abscissa. Straight lines have been drawn through the points because it has been shown [5] previously that the logarithm of the life is a linear function of the load for rayon cords under the conditions of this test. The solid lines give the lives at various loads in grams per denier. The intersection point of these lines determines the load of 0.34 gram per denier at which the lives of the cotton and the rayon cords are equal. Above this load the rayon has the longer life and below this load the cotton has the longer life. The lives at fractions of their oven-dry breaking tensions are given by the dotted line for rayon and the solid line for cotton. Their

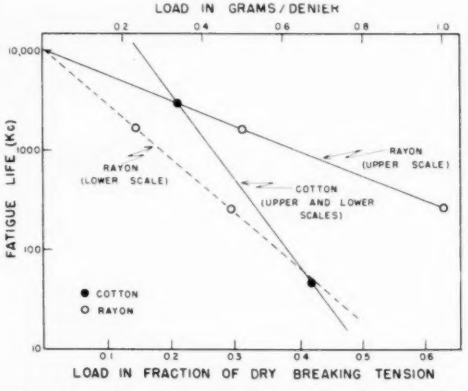

FIG. 3. *Effect of load in grams per denier and in fraction of oven-dry breaking tension on fatigue life for cotton and rayon.*

TABLE IV. Effect of Twist Structure on Life in Various Tests

Twist				D. B. Tester			
Single	Ply	Denier	Conditioned breaking load in kg.	1 g./den. Undipped	35% conditioned breaking load Undipped	Dipped	Mallory tester
11.0Z	11.0S	3,690	10.3	(1.00)	(1.00)	(1.00)	(1.00)
8.8Z	11.5S	3,720	10.4	.64	.70	.76	.84
9.1Z	9.6S	3,580	11.0	1.35	.57	.60	.59
8.9Z	7.7S	3,460	11.7	1.74	.52	.57	.09

lives are equal at 0.4 of their dry breaking tensions (0.64 gram per denier for cotton and 1.3 grams per denier for rayon). The assumption of a straight line for cotton cannot produce any appreciable error in determining the intersection points for the curves because the experimental values for cotton are nearly at the intersection points.

The lives of cords with various twist structures made from the same type of rayon were measured on the dynamically balanced fatigue tester with weights on the cords of 1 gram per denier and 35% of the conditioned breaking load of the cords. The results of these measurements are given in Table IV. At a load of 1 gram per denier the life tends, for the most part, to increase with decreasing twist, but at 35% of the conditioned breaking load the life decreases with decreasing twist. Dipping these cords had little effect on the relative fatigue lives although the absolute lives were increased about 60%. The relative lives of these cords on the Mallory tester [4], for which the cords are imbedded in rubber, are given in the last column of the table. These values correlate much better with the values of the new tester at 35% of the breaking load than with those at 1 gram per denier. It seems possible that the very low value for the lowest-twist cord on the Mallory tester may be caused by buckling of the cord during the compression part of the cycle.

Summary and Conclusions

A fatigue tester for dipped and undipped tire cord has been designed which makes use of out-of-phase stretching and relaxing of two cords against a weight hung on their lower ends. This design permits the use of a high stroke in a lightweight machine and this high stroke provides a reasonably short life without resort to excessively high temperatures or loads.

Relative fatigue ratings on this tester correlate better with the performance that we would expect in tires when the cords are loaded at a fraction of their breaking strength than when they are loaded at 1 gram per denier. A more effective way to use this tester for comparing the relative fatigue properties of cords is to compare their lives at various loads.

The fatigue life of rayon cords is higher than that of cotton cords at high loads, but the order is reversed at low loads. Dipping the cords has no effect on the relative fatigue behavior of cotton and rayon cords or of rayon cords with various twist structures, although it may change the absolute level for both types of cord.

Acknowledgment

The writers wish to acknowledge the assistance of Mr. J. P. Cann and Mr. C. H. Semones in constructing this tester, and of Mr. R. E. Spain for making fatigue tests.

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(*Manuscript received June 9, 1949.*)

Levelness of Acid Wool Dyes: The Application of Laboratory Tests to Production

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Abstract

A quantitative laboratory method for evaluating levelness of acid wool dyes is described. The procedure consists of running half of a normal yarn-dye cycle and then making additions of white yarn and dye liquor equal in amount to those in the original batch. The second half of the cycle is then run, and the yarns are removed. Reflectances of the two dyed yarns are determined on a G. E. recording spectrophotometer and a "levelness index" is calculated as the ratio of dye concentration on the yarn added at the mid-point of the cycle to that on the yarn started at the beginning of the cycle.

The technical background of the test method is outlined and the results of tests on representative dyes are tabulated. It is shown that the test method has sufficient flexibility to permit examinations of the effects of dyeing variables on levelness. An example is cited showing the effect of salt concentration on levelness of Alizarine Cyanine Green CG ex. (C. I. 1078).

The example above is applied to plant production, and the levelness of 500-pound Hussong stock-dyed batches is evaluated by spectrophotometer reflectances, converted to dye concentration, of stratified samples from the batches of stock. It is shown that the coefficient of dye concentration variation among the 8 samples from a plant batch is proportional to the laboratory "levelness index."

Laboratory Test Method for Evaluating Levelness

The evaluation of dye levelness has been the subject of much previous consideration. Gunther [1] describes several methods which have been used for the evaluation of leveling agents and gives a bibliography of 28 references. He mentions a method for the evaluation of migration of dyes and also the use of the spectrophotometer for the rating of exhaust liquors.

Ris [5] describes a graphical method for showing the dyeing properties of acid wool dyes. His method separates the two factors of exhaust rate and migration rate. From the data provided, the dyeing properties of a series of dyes may be qualitatively compared.

The method described in this paper differs from the above method in that it does not separate exhaust and migration rates because its purpose is to indicate the actual operating properties of the dyes in production, where those factors are not separated. Furthermore, through the use of the spectrophotometer a quantitative evaluation of levelness is deduced by a general method which is flexible and suited to almost any dyeing procedure.

Two laboratory dye baths of 500 cc. each, containing salt, acid, and the dye to be tested, are prepared. The two dye liquors are brought to a boil; a dry 10-gram wool skein is entered into one of them and worked for 22½ minutes. At the end of that time the two dye liquors are mixed together in a 1,000-ml. beaker and both the dyed and the undyed skeins are entered and worked for an additional 22½ minutes. The skeins are removed and dried, and their reflectances are measured on the spectrophotometer at the wave length of maximum absorption. In order to get the original reflectance, an undyed skein of the same lot is also measured.

Using tables for the conversion of reflectance to K/S values, the levelness index, "L. I.," of the dye

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tested is defined mathematically as follows:

$$\text{L.I.} = \frac{\Delta(K/S)_2}{\Delta(K/S)_1},$$

where $\Delta(K/S)_2$ is the difference between K/S values for the skein dyed for the final $22\frac{1}{2}$ minutes only and an undyed white skein; and $\Delta(K/S)_1$ is the difference between K/S values for the skein dyed for 45 minutes and an undyed white skein.

That this ratio is the ratio of dye concentration on the two skeins is proved by the following:

A—According to Kubelka and Munk [2], monochromatic reflectance is defined by the relationship

$$R = 1 + (K/S) - [(K/S)^2 + 2(K/S)]^{\frac{1}{2}},$$

where K is the absorption coefficient or fraction of the incident energy lost by absorption per unit thickness of material, and S is the scattering coefficient or fraction of incident energy loss due to scattering per unit thickness of material.

It is assumed that the material being measured is thick enough to show no background color and that the illumination is diffuse.

B—Solving the above equation for K/S:

$$K/S = \frac{(1 - R)^2}{2R}.$$

C—Pineo [4] and others [3, 6] have demonstrated the fact that a plot of the function $(K/S) = \frac{(1 - R)^2}{2R}$ is linear with respect to the concentration of dyestuff on the fibers. Assuming a white ground,

$$K/S = kC,$$

where k is a constant, and C is the concentration of dye on the fiber.

D—In the case of all real fibers, however, there is a certain amount of absorption which causes the fibers to appear less white than the theoretical white ground. The writers mention that in these cases the concentration of dye present is proportional to the difference between the value of (K/S) for the dyed fibers and that for the undyed fibers:

$$(K/S)_D - (K/S)_U = \Delta(K/S) = kC,$$

where the subscripts D and U refer to the dyed and undyed fibers, respectively.

E—From the above, it is possible to calculate a levelness index which is defined as the ratio of the dye present on the skein added at the midpoint of the cycle to the dye present on the skein added at the start. The more nearly this number approaches 1 the greater the leveling tendency of the system. The resulting equation is

$$\frac{(\Delta K/S)_{22.5}}{(\Delta K/S)_{45}} = \frac{k_1C_1}{k_2C_2}.$$

F—Since the same dye is on both skeins, $k_1 = k_2$ and, therefore,

$$\frac{(\Delta K/S)_{22.5}}{(\Delta K/S)_{45}} = \frac{C_1}{C_2} = \text{L.I.}$$

Results of Laboratory Test

In order to illustrate the application of this method, a series of acid dyes was tested for a comparison of levelness indices and for the effects of varying certain dyeing factors. Table I illustrates the differences among the levelness indices of a few acid dyes, all skeins dyed under the same conditions using 5% anhydrous sodium sulfate (on the weight of the wool) and 4% acetic acid. In all cases the dye bath was made up with 0.1% dye (on the weight of the fiber). Note that the lowest values of levelness index occur with the Cyanine Green and Cloth Red, which are known to be poor in leveling qualities. A perfectly level dye would, of course, have a levelness index of 1.00. At the other extreme, the minimum value of levelness index, indicating no leveling tendency, would theoretically be 0.333. This would be the case if all of the first portion of dye plus one-half of the second portion were exhausted on the skein dyed for 45 minutes and only one-half of the second portion of dye were on the skein dyed for $22\frac{1}{2}$ minutes. This would give a ratio of dye concentration on the two skeins of 1/3. Two series of repeat tests on the dyes in Table I under the same conditions show reproducibility of the L. I. within 8% of the mean value. That is, in the case where the levelness index is 0.479, the range of the three tests does not exceed 0.479 ± 0.019. Table II shows the effect of dye concentration and salt content on the levelness index of Alizarine Blue SAP (another commercial form of C. I. 1054).

The data bear out the common knowledge that the presence of salt improves the levelness properties of the acid dyes. In each case the dyeings made with $2\frac{1}{2}$% and 5% of salt are significantly better

TABLE I. LEVELNESS INDICES OF SOME ACID WOOL DYES
(5% Na_2SO_4 AND 4% CH_3COOH; 0.1% DYEING, 50/1 WATER/WOOL RATIO)

Dyestuff	For maximum absorption (mμ)	Dyeing time (min.)	Reflectance	$(K/S)_D$	Undyed wool R_U	Undyed wool $(K/S)_U$	$(K/S)_D-(K/S)_U$	L. I.
Alizarine Irasol RD (C. I. 1073)	577	22.5	21.8	1.403			1.282	
		45	20.5	1.542	61.4	.1213	1.421	0.903
Cloth Red BN (C. I. 262)	536	22.5	9.3	4.423			4.253	
		45	4.4	10.386	56.3	.170	10.216	0.416
Anthraquinone Blue BN (C. I. 1054)	650	22.5	17.7	1.913			1.840	
		45	15.2	2.365	68.4	.073	2.292	0.803
Alizarine Cyanine Green CG ex. (C. I. 1078)	613	22.5	23.4	1.254			1.164	
		45	14.5	2.521	65.7	.0895	2.431	0.479
Pontacyl Fast Lt. Yellow 3G (C. I. 636)	405	22.5	12.0	3.227			2.491	
		45	9.3	4.423	31.7	.736	3.687	0.675
Alizarine Direct Blue A2G (C. I. Pr. 10)	634	22.5	26.8	.997			.923	
		45	23.4	1.254	68.3	.0736	1.180	0.783

TABLE II. EFFECT OF DYE CONCENTRATION AND SALT CONTENT ON THE LEVELNESS INDEX OF ALIZARINE BLUE SAP (C. I. 1054)
(LEVELNESS INDEX AT λ = 610 mμ; 50/1 WATER/WOOL RATIO, 4% CH_3COOH)

Anhydrous Glauber salt in dye bath (%)	Dyestuff concentration (%)	Dyeing time (min.)	Reflectance	K/S	$(K/S)_D-(K/S)_U$	L. I. $\Delta(K/S)_2/\Delta(K/S)_1$
—	0.0	—	63.2	.107	.107	—
0	0.1	22½	21.8	1.403	1.296	
		45	13.3	2.826	2.719	0.476
2½	0.1	22½	19.8	1.624	1.517	
		45	15.7	2.263	2.156	0.705
5	0.1	22½	20.2	1.576	1.469	
		45	15.6	2.283	2.176	0.676
0	0.5	22½	6.6	6.609	6.502	
		45	3.3	14.168	14.061	0.463
2½	0.5	22½	5.7	7.800	7.693	
		45	4.4	10.386	10.279	0.748
5	0.5	22½	5.3	8.460	8.353	
		45	4.0	11.520	11.413	0.732
0	2.0	22½	2.1	22.820	22.713	
		45	1.6	30.258	30.151	0.753
2½	2.0	22½	2.0	24.010	23.903	
		45	1.7	28.420	28.313	0.844
5	2.0	22½	1.9	25.325	25.118	
		45	1.6	30.258	30.151	0.834

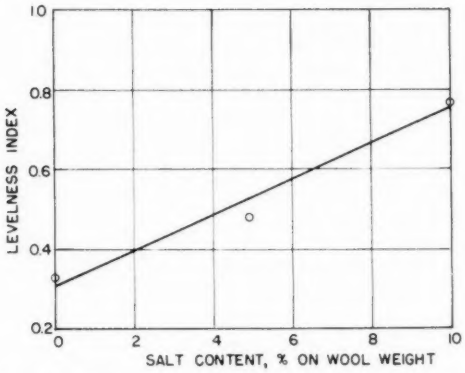

FIG. 1. *Effect of salt concentration on levelness index of Alizarine Cyanine Green CG ex. conc.*

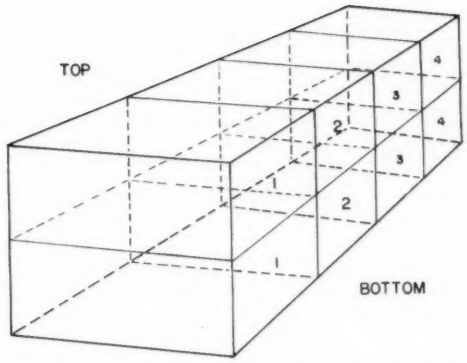

FIG. 2. *Diagram of division into strata for dye levelness sampling. 500-lb. Hussong batch of stock-dyed wool.*

that those made without salt. It is also interesting to note that there is no significant improvement in levelness with the change from $2\frac{1}{2}\%$ to 5% salt content.

Within the range of reflectances obtained from 0.1% to 2% of dye it appears that the heavier shades show greater levelness than the lighter shades. Laughlin [3] has indicated that K/S is proportional to dye concentration, provided the reflectance is 2% or more. The 2% dyeings in this instance fall below the value in some cases, which makes the reliability of the results for the very dark shades somewhat doubtful. The visual examination, however, of slight differences in dye concentration on dark shades is more difficult than on the light shades, and the skeins appear to be more level in dark shades.

It will be noted that this method of evaluating levelness does not separate factors of initial migration rate. Rather, the two are combined in an undefined manner to give the practical effect of "levelness" or the lack thereof.

Comparison of the levelness indices with dyeing experience indicates that a levelness index range of 0.6–0.7 is a dividing region and that dyes having indices lower than 0.6 are not suitable for skein dyeing, whereas those with indices above 0.7 are generally suitable for skein dyeing, mechanical factors being adequate.

TABLE III. EFFECT OF SALT CONCENTRATION ON LEVELNESS INDEX OF ALIZARINE CYANINE GREEN CG EX. CONC. (0.5% DYEINGS, 4% ACETIC ACID, 50/1 WATER/WOOL RATIO)

Salt content	Levelness index
0	0.324
5% on wool weight	0.479
10% on wool weight	0.766

That the levelness index of a stock dyeing color, Alizarine Cyanine Green CG ex. conc., can be significantly affected by the salt content of the dye bath is shown in Table III and Figure 1. With no salt in the bath, the levelness index is very low, even for a stock dye color, but with 10% salt the dye is brought to the threshold of skein dyeing levelness. It will be observed that the levelness index when no salt is used is 0.324. This is lower than the theoretical minimum mentioned above. This situation may be a reflection of the 8% range within which the test is reproducible (0.324 ± 0.015). On the other hand, it is possible that in practical cases a slightly lower value than 0.333 could be achieved because of the alkalinity of the scoured skeins before they enter the dye bath. The yarn entered for the second $22\frac{1}{2}$ minutes would take a little time to approach pH equilibrium with the bath and neutralize its alkalinity, while the 45-minute skein is already acid and starts immediately to take up dye after the addition. It was desired to determine how this test would correlate with practical mill experience, and for that evaluation the following procedure was used.

Method of Evaluating Levelness in Production

The levelness of a large batch of wool is defined as the uniformity of color of wools at all points in

TABLE IV. LEVELNESS EVALUATION OF 500-LB. HUSSONG DYEINGS (0.5% ALIZARINE CYANINE GREEN CG EX. CONC.)

Sample	K/S (no salt)	K/S (5% salt)	K/S (10% salt)
1 Top	3.770	3.520	3.718
2 Top	4.001	2.970	3.227
3 Top	2.568	2.718	3.405
4 Top	1.945	3.127	3.560
1 Bottom	3.642	3.062	4.366
2 Bottom	1.344	2.692	2.826
3 Bottom	1.171	3.094	3.193
4 Bottom	3.094	3.481	3.600
$\bar{X}$ = means K/S	2.692	3.083	3.487
$\bar{X}_\Delta{}^2$	0.900120	0.081347	0.180223
σ	0.300	0.285	0.134
C.V. $= \frac{\sigma}{\bar{X}}$	0.111	0.092	0.038

the batch. This being the case, the dye concentration on wools from different portions of the batch can be used as a measure of levelness provided there is only one dye used. Accordingly, a 500-lb. Hussong batch of dyed stock, physically in the form of a rectangular solid, is sampled from the 8 portions shown in Figure 2. A random sample taken from each stratum is dried and carded, and its reflectance is measured at the wave length of maximum absorption of the dye being examined. Reflectances are converted to K/S units and dye concentrations in the same manner as in the laboratory tests described above. The standard deviation of the 8 values is then calculated and expressed as the coefficient of variation, "C.V.," which is the standard deviation expressed as a fraction of the mean K/S. In this case, the levelness is inversely proportional to the coefficient of variation—that is, the lower the coefficient of variation the more level the batch. For instance, zero coefficient of variation indicates perfect levelness.

Results of Mill Levelness Tests

500-lb. Hussong dyeings were made with 0.5% Cyanine Green, 20:1 water/wool ratio, and 4% acetic acid at 0%, 5%, and 10% salt contents. The coefficients of variation of the three batches are given in Table IV and Figure 3.

The batches, with different salt contents, may be described in a qualitative way as follows:

A—The batch with no salt and C.V. = 0.111 was extremely unlevel, showing readily visible patches of almost undyed wool.

TABLE V. RELATION BETWEEN 1/C. V. AND L. I. (DATA FROM TABLES III AND IV)

Salt content	C. V.	1/C. V.	$\frac{1}{9}$C. V.	L. I.	L. I. 0.324
0	0.111	9.00	1	0.324	1
5%	0.092	10.90	1.21	0.479	1.47
10%	0.038	26.95	2.90	0.766	2.36

B—The batch with 5% salt content and C.V. = 0.092 showed considerable improvement, with no wools completely undyed, but there was a large variation in depth of shade from point to point.

C—The batch with 10% salt content and C.V. = 0.038 showed satisfactory levelness, with only small visual variations in depth from point to point.

Table V shows the extent of agreement between the levelness index and C.V. for this case. The inverse proportionality is removed by determining the reciprocal of C.V.; then the lowest values of 1/C.V. and L.I. are converted to unity and the successively higher values are expressed as multiples thereof. The fourth and sixth columns indicate the similarity of the relationships. It will be noted that they follow the same general trend. The data are insufficient to form a base for the assumption of a

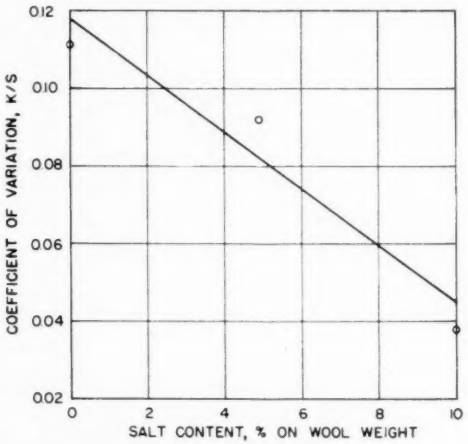

FIG. 3. *Effect of salt concentration on coefficient of variation, 0.5% dyeings of Alizarine Cyanine Green CG ex. conc., 500-lb. Hussong stock-dyed batches.*

linear relationship between salt content and L.I. and between salt content and C.V. One would anticipate that beyond a certain point a given increase of salt content would not produce a proportional improvement in levelness. The curves, therefore, might be expected to become asymptotic to some value of L.I. at higher salt contents. For the purpose of this preliminary exploration, however, the straight line is drawn as a first approximation.

Conclusions

It has been demonstrated that a quantitative laboratory test for dye levelness gives results which are consistent with dyeing experience and can be correlated with the levelness of stock-dyed wools. It has also been shown that the effect of dyeing variables can be examined by means of the techniques described. The effect of salt content on dye levelness in certain applications has been explored in a preliminary way, showing a trend which is in agreement with dyeing experience. The precise nature of the relationship between salt content and levelness has not been worked out in complete detail owing to the limited amount of data obtained.

Acknowledgment

The authors express thanks to Mr. J. L. Barach and Miss E. Friede, Chief of the Physical Research Section and Research Physicist, respectively, at Alexander Smith & Sons Carpet Company, for assistance in the method of levelness evaluation on production batches.

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(*Manuscript received August 5, 1949.*)

Laboratory Techniques

Examination of Textile Fibers by the "Dispersion Staining" Method

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Abstract

The "dispersion staining" method is used for observing textile fibers in colors which aid in the determination of their structure and in their identification. Fibers which are classified as striated or microscopically structureless are distinguished by this technique without the need for any special preparation of the fiber. A sample is mounted in a liquid of high dispersion which has a refractive index near that of the fiber and the fiber is identified by the resulting coloration, using an ordinary compound microscope set-up for dark-field illumination.

WHEN certain textile fibers are examined microscopically, their size, shape, and characteristic markings permit the observer to identify them. However, positive identification of fibers or proof that two fibers are similar is more difficult when the fibers are regular in outline and free from significant markings. In studying structure, the importance of various optical properties—such as refractive index and relative dispersion—is recognized in present methods of fiber examination [8, 10]. These optical properties can be observed as the color phenomenon produced by the Christiansen effect [2], which occurs in petrographic immersion methods of studying refractive index. This coloration occurs when a solid is immersed in a liquid having nearly the same refractive index as the solid, with at least one of the materials having strong dispersion characteristics. Controlled use of this effect has been applied microscopically with transmitted, dark-field illumination and is termed "dispersion staining" [3, 4, 5, 6]. This technique makes transparent materials differing slightly in optical properties appear to be different in color, even though each material is clear and colorless. The present paper is a study of the application of "dispersion staining" to the examination and identification of textile fibers.

Method

The amount of apparent color produced by "dispersion staining" is dependent upon the combination of condenser, objective, and dark-field stop used with the microscope. The following combination produces strong coloration, and it is necessary to adhere to each of the details in order to obtain maximum color intensity:

1. Condenser—achromatic, N.A. 1.40, with top element removed to reduce N.A. to 0.59.
2. Objective—achromatic 10.25-mm., 20 ×, N.A. 0.40, with anti-reflection coated lens.
3. Eyepiece—10 × Huygenian.

The 10.25-mm. objective is a metallurgical objective adjusted for a 215-mm. tube length rather than for the normal 160-mm. one of most biological and other microscopes; however, this difference is not critical in observing the "dispersion staining" colors. On the other hand, the numerical aperture of the objective is critical and thereby excludes the use of the 8-mm., 21 × achromatic microscope objective with N.A. 0.50, which is adjusted to the normal 160-mm. tube length.

Dark-field illumination is obtained by placing a 17-mm. dark-field stop in the slotted ring below the condenser. The condenser is adjusted up or down until fibers, mounted as described below, appear brightly colored against a dark background. If the correct diameter stop is not available, one can be made by cementing a circle of black cardboard of the correct size to the center of a smaller-diameter stop. A microscope lamp containing a 6-volt, 108-watt ribbon filament bulb is focused to produce even illumination. A blue daylight glass filter, polished on both sides

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for maximum transmission, should be used with the microscope lamp. Fibers can also be examined with polarized light by use of a cap analyzer over the eyepiece. This analyzer should be oriented, first, to pass light vibrating parallel to the long axis of the fiber and, second, perpendicular to the long axis.

Fibers are mounted between a clean glass microscope slide and a cover glass in a liquid having a high relative dispersion and an index of refraction near that of the fibers to be studied. Immersion liquids intermediate in refractive index between diethylene glycol monobutyl ether (n_D 1.43) and cinnamaldehyde (n_D 1.62) can be made by mixing appropriate amounts of these liquids. The index of refraction may be checked accurately with a refractometer.

Identification of Fibers

An unknown fiber can be compared with known fibers by using the above technique. It would be extremely unlikely that the index of refraction, the difference in index for different wave lengths of light, and the relation between optical properties lengthwise and across the fiber would lie so nearly alike as to produce the same color unless the fibers were identical. If the fibers have been dyed, the "dispersion staining" colors can be made to appear as a halo or colored Becke line outside the fiber by focusing the microscope above or below the sharp focus position at the edge of the fiber. Slight variations in color along a fiber indicate corresponding variations in refractive index. Such variations have been described by Fox and Finch [7]. The regenerated-cellulose rayons—viscose and cuprammonium—can be separated as a group from other fibers, but the refractive index may vary almost as much from one lot to another as from one type to another [8, 9]. The use of the cap analyzer will aid in their differentiation.

Color intensity is decreased if a fiber contains a delusterant. When working with delustered fibers, it is convenient to cause the color to move outside the fiber by focusing up or down from the point of sharpest focus.

Systematic Analysis of Fibers

A laboratory concerned with the routine identification of fibers will find it worth while to devise a systematic scheme of analysis. Three immersion liquids having indices within the refractive index range of the fibers encountered normally will be adequate. Other immersion liquids may be added to the collection for identification of fibers with extreme optical properties, or for identification of specific isotropic fibers. The following procedure is an example of such a scheme of analysis:

TABLE I. FIBERS AND "DISPERSION STAINING" COLORS WITH CAP ANALYZER PARALLEL TO LONG AXIS OF FIBER

Fiber	Refractive index of the liquid 1.550	1.524	1.580
Acetate	White	White	White
Cuprammonium	Reddish purple	Yellow	White
Nylon	Yellow	White	Blue
Silk	Yellow, slight red	White	Orange, red, yellow
Viscose	Blue, slight red	Yellow	Blue-white

Fibers are classified first by structure in ordinary bright-field illumination [1], then by the color produced in a 1.550 immersion liquid with dark-field illumination. If a yellow color is observed with the cap analyzer in parallel position, a second slide is made with the fiber in a 1.580 immersion liquid. Colors other than yellow indicate that the next slide should be made with a 1.524 immersion liquid. Following this scheme of analysis, the characteristic colors produced by some of the fiber samples examined in this laboratory, with the cap analyzer in the parallel orientation, are shown in Table I. Acetate, for example, appears white in the three immersion liquids normally used; however, it is blue with slight red in a 1.478 liquid with the cap analyzer in parallel position. A different series of colors for each fiber is obtained with the cap analyzer in the perpendicular position to the long axis of the fiber. Slight variations from the colors listed in Table I will depend upon the source and treatment of the material as well as upon the technique used in applying this method.

"Dispersion staining" thus offers a means of examining and identifying fibers singly and in mixtures. The colors obtained under dark-field illumination with this combination of immersion liquids and with different orientation of the cap analyzer will distinguish fibers which otherwise appear similar in ordinary examination with the microscope.

Acknowledgment

The authors wish to acknowledge the kind assistance offered with the textile fibers for this investigation: E. I. du Pont de Nemours and Company, Rayon Technical Service Section, for viscose, acetate, and

nylon yarns; American Bemberg Company for cuprammonium rayon yarns; United States Testing Company for silk yarns; and Linen Thread Company for jute yarn.

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(*Manuscript received June 2, 1949.*)

Diagonal Sectioning Technique for Studying Fabrics

M. R. Pesce* and A. S. Wrigley*

THE IMPORTANCE of fabric geometry considerations in the design of functional fabrics was stressed some time ago in the works of Peirce [4] and more recently by Backer [1] and Pollitt [3]. The geometric assumption that yarns can be considered as flexible circular cylinders has permitted the mathematical presentation, in a general way, of the physical characteristics of textile materials. However, in the study of high-sley fabrics the yarn distortion resulting from the extreme weave tightness does not justify extensive computations based on these simplified considerations.

The yarn structure as it actually exists in a fabric can be presented and studied by microscopical techniques such as cross-sectioning the material at right angles to the warp and filling yarns and in planes normal to the fabric surface. In order to reveal the three-dimensional aspects of the fabric interstices, successive sections above, through, and below a cross yarn would be necessary. However, serial sectioning must be done painstakingly and at best it furnishes only a discontinuous picture of the interyarn spaces.

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By using a diagonal sectioning technique, it is possible to obtain, with only one section, an uninterrupted sequence of views through and between alternate yarns.

Diagonal sections can be prepared by embedding the fabric in plasticized methyl methacrylate monomer [2], mounting the polymerized resin block in a biological microtome, and orientating the specimen holder so that the fabric is sliced in a plane tilted at a small angle to the plane normal to the warp (or filling) direction.

An illustration of diagonal cross sections is presented in Figure 1. The sections were cut from a tightly woven experimental Oxford material. Successive but slightly overlapping sections were photographed and then assembled in continuous strips.

The diagonal sections illustrate at a glance the marked differences which exist in the warp and filling directions of the fabric structure. The close packing of the pairs of warp yarns (woven as one) makes it difficult to distinguish between these adjacent ends. Appreciable cross-sectional changes take place in the warp yarns as they pass over and under the filling yarns. At the interfilling spaces, the alternate warp-yarn pairs are crowded together (A in the

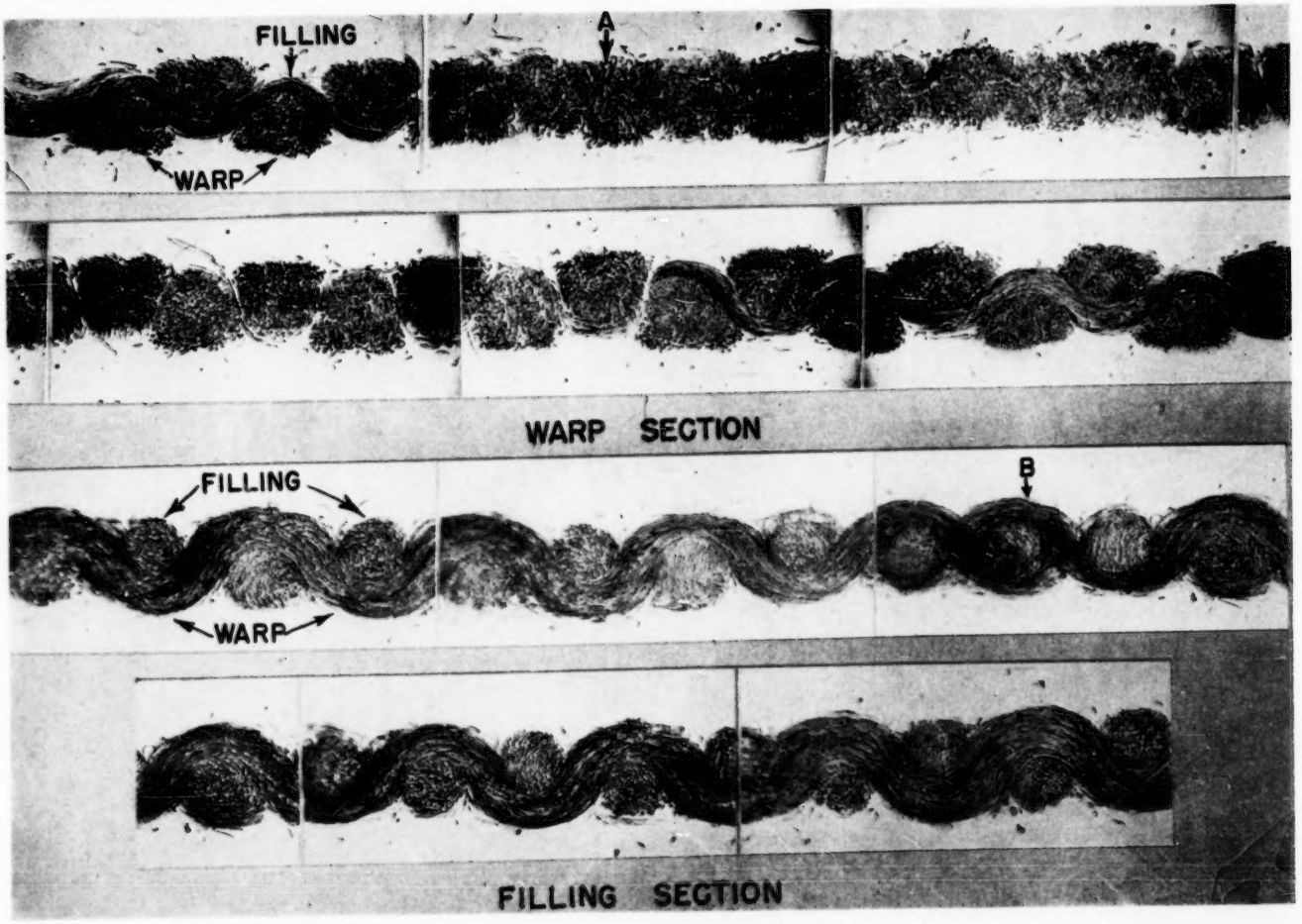

FIG. 1. *Oxford fabric—diagonal cross sections. Magnification 40 ×.*

figure) and the only indication of yarn structure is a gradation of densities between alternate yarn centers.

The filling cross-sectional view shows that inter-filling contact is prevented owing to the tight warp packing. In fact, at one point (B in the figure) along the section, portions of two alternate warp yarns are seen to be in the same plane. Finally, the relative size and crimp of the warp and filling yarns are evident upon comparison of the two sections.

Judging from the usefulness of this simple technique in Quartermaster studies of fabric structure, we believe that others may be interested in knowing about it.

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(Manuscript received July 14, 1949.)

Book Reviews

An Introduction to Textile Bleaching. J. T. Marsh. New York, John Wiley & Sons, 1949. 512 pages; 32 plates. Price, $6.50.

(Reviewed by George H. Wood, The Apponaug Company, Apponaug, Rhode Island)

The purpose of this book is, according to the author, to record the principles and developments of the present state of textile bleaching.

He has written it not only as a guide for those just entering the industry but to bring together for the experienced bleacher the practical and scientific knowledge of the art.

Although the title is *An Introduction to Textile Bleaching*, the book actually "is concerned with the occurrence and properties of the various textile fibers and the methods adopted for their purification." It is divided into six parts.

Part I gives a classification of fibers, with details of chemical constitution, derivatives, chemical reactions, and physical properties. All types of fibers are discussed—animal, vegetable, and mineral; synthetic, natural, and regenerated.

Part II deals with wetting agents, detergents, water softeners, and assistants that are used in processing yarn or piece goods before the actual bleaching operation. The chemistry of these compounds is discussed, as well as their practical value.

Part III is a description of the scouring and bleaching of cellulosic fibers, covering older methods as well as newer. The most used method—the hypochlorite bleach—is especially well covered. The principles of bleaching have received more prominence perhaps than the practice, and this is a good feature, for although the practice has been well founded there has been a tendency to treat the scientific knowledge of bleaching lightly.

Part IV covers the scouring and bleaching of wool and silk in detail, bringing together the accumulated experience of both the scientific and the industrial points of view. It also includes references to casein fibers and nylon.

Part V takes up the drying of textiles. The mechanical removal of excess water and drying by evaporation are fully described, with diagrams of the apparatus used.

Part VI gives tests for damage. "The term *damage* in this connection is obviously wider than the appearance of gross mechanical defects, and includes certain modifications of the material which may be acceptable to the consumer within certain limits." Scientific control and guarantees of satisfaction require accurate methods of measurement. The physical and chemical test methods given here are becoming more and more important to the textile industry for proper evaluation of performance of the fibers and fabrics in actual use.

The bibliography, name index, and subject index will assist the reader in locating any subject of special interest. The diagrams, tables, and illustrations are a valuable part of the book.

The experienced mill man as well as the beginner should find this book of assistance in obtaining a better understanding of the principles and practice of scouring and bleaching.

Die Unterscheidung der Textilfasern. Bruno Luniak. Mitteilungen aus dem Institut für Textilmaschinebau und Textilindustrie an der Eidgenössischen Technischen Hochschule in Zurich. Second enlarged edition. Zurich, Verlag Leemann, 1949. 192 pages. Fr. 30.—

(Reviewed by Richard O. Steele, Textile Research Institute)

This is an excellent handbook for everyone who is concerned with the identification of textile fibers or the analysis of fiber mixtures. Concisely, yet in sufficient detail, it explains how a fiber sample should be cleaned and, if necessary, stripped of dye; how its components may be qualitatively identified and how they may in most cases be quantitatively determined.

No set "qualitative scheme" is provided, giving "either-or" tests which lead unfailingly—on paper at least—to a proper identification. Aside from a somewhat greater unity which this might have provided, it is not really missed. The properties of the various classes of fibers are tabulated so that distinguishing characteristics of the fibers within a given class can be readily found.

The chief emphasis of the book is on the use of the microscope for qualitative examination. Over half the pages are devoted to this, including 48 pages for the reproduction of 288 photomicrographs. The microscopes and photomicrographic equipment described are all of Continental manufacture, but their principles and the techniques required are equally useful with American instruments. The emphasis on the use of the microscope for observing both the morphology of fibers and their action with stains and reagents is properly placed in view of the absolute necessity of making such observations in the course of most identifications.

The high-quality photomicrographs are well reproduced and include numerous examples of the important natural and synthetic fibers as well as a large number of natural and synthetic fibers which are less frequently encountered, including synthetics which are as yet in the experimental stage. American synthetic fibers are satisfactorily represented.

Such a collection of photographs should be an excellent introduction to fiber identification for beginners, as well as a useful reference for more experienced technicians. However, with such aids as this available, fiber identification can appear deceptively simple, and a word of warning is perhaps in order. No photograph can be as satisfactory as a microscopic comparison of an unknown with a known sample, and no description of a chemical test can substitute for actual physical familiarity with the procedure and the results to be expected.

For quantitative determinations, the author recommends that the fiber to be identified be removed from the test sample with a suitable solvent, using a separate sample for each fiber in the mixture. Tables showing the solubility of the various classes of fibers in selective solvents are given.

For many of the tests used there are references to the pertinent German, English, Swiss, and American literature, including references as late as the first half of 1948. However, it is disappointing to have to report that the book has no index, which would have considerably enhanced its usefulness. Its omission in a work of this sort seems inexcusable. The physical make-up of the book is very satisfactory, and few typographical errors were observed.

Beiträge zur Oxydation von Cellulose mit Stickstoffdioxyd. Askar Pfeiffer and D. Krüger. Weinheim Bergstr. and Berlin, Verlag Chemie, GmBH, 1949. 85 pages. Price, $2.70.

(Reviewed by O. A. Battista, American Viscose Corporation)

This book is a contribution to the chemistry of cellulose oxidation by nitrogen dioxide. It is divided into two sections: (I) "The Oxidation of Regenerated Cellulose Staple Fibers and Their Resulting Properties," by Dr. O. Pfeiffer, and (II) "Salt Formation and Other Chemical Reactions of Nitrogen Dioxide-Carboxy Cellulose," by Deodata Krüger.

The workers state that they are aware of the exhaustive studies by Kenyon and coworkers in the United States on the oxidation of cellulose. However, whereas most of the work by the American workers was conducted on purified cottons, the German scientists have investigated rather comprehensively the oxidation of regenerated or hydrate cellulose by nitrogen dioxide, the bulk of their work having been carried out on viscose rayon in staple form. They have given special emphasis to the consideration of properties which could be utilized for textile manufacturing and related industrial uses, and in this respect the book contains a wealth of useful data.

Numerous chemical and physical tests were performed on the derivatives. For example, the authors specify that it is possible to correlate the swelling and copper number of their carboxy celluloses with tensile strength, carboxy content, and degree of polymerization. Conditions were found under which tensiles can be held constant in spite of an increase in copper number.

Upon oxidizing rayon staple with NO_2, the resulting products were found to have the following general properties: (1) carbon dioxide was eliminated upon heating the product in dilute acid; (2) alkali solubility was very high; there were (3) changes in swelling, (4) increased resistance to wetting, (5) increased brittleness of the dried product, (6) increase in copper number (all products had a minimum copper number of 5), and (7) lower degree of polymerization.

In addition, the formation of mono- and multivalent salts of the carboxy cellulose products from rayon staple was studied exhaustively with the object of using these reaction products in technical textile applications.

In so far as the book deals specifically with carboxylated hydrate cellulose derivatives, their chemical

reactivity, and physical properties, it is to be recommended as of particular value for workers engaged in the *chemical research* phase of textiles, even though the basic chemistry involved has been covered exhaustively by Kenyon and his associates in the United States.

Kunststofftechnisches Wörterbuch (Plastics Technological Dictionary). A. M. Wittfoht. München, Carl Hanser Verlag, 1948. 316 pages. Price, 12.–DM.

(*Reviewed by Eugene Pacsu, Princeton University*)

This German-English and English-German dictionary was compiled and published to meet the everyday practical requirements of American, British, and German experts in the plastics industry who are concerned with technical terms and expressions in both languages. Original explanations are frequently given and the goodly number of drawings should be of considerable help in illuminating certain definitions. In the appendix a list of general and technological abbreviations, as well as conversion tables for the different systems of measures, is given.

The book should prove to be a useful investment for anyone interested in the German scientific, technical, and patent literature on plastics.

Modern Plastics Encyclopedia, 1949. New York, Plastic Catalogue Corporation, 1949. 1,371 pages and charts. Price, $5.00.

The *Modern Plastic Encyclopedia* continues to be the only complete guide to the application of all types of plastic materials. The 1949 issue brings the material in this field up to date in most respects, with several improvements in the method of presentation.

To begin with, there is an 8-page glossary of uncommon technical terms for edification of the nontechnical reader. The section on "Plastics in Use" has been expanded to 194 pages from the 60 pages in the 1948 edition. The Technical Data section includes a valuable "Survey of the Properties of Plastics," which aids the reader in finding the properties of commercial plastic materials. Finally, the 12 annually revised charts have been incorporated into the Technical Data section in page form. These improved features, together with the regular sections on materials, coatings, films and sheetings, fibers and fabrics, laminates, and processing methods, help the 1949 edition to maintain the high standards of previous issues.

The present book is profusely illustrated with excellent pictures of some of the million-and-one products of the plastic art. Consistent readers will recognize may of these as repeat items described in previous volumes.

The editors apparently believe, and rightly so, that a picture is worth a thousand words of descriptive material.

Although the new volume is somewhat shorter than the previous one, it is no less complete in its technical coverage. The reduction in size is due to elimination of the catalog of stock molds and over 100 pages of advertizing which appeared in the 1948 edition. These omissions do not seriously detract from the book.

Fundamental Processes of Dye Chemistry. Hans Edward Fierz-David and Louis Blangey, Technical Institute, Zurich, Switzerland. Translated from the Fifth (1943) Austrian Edition by Paul W. Vittum, Eastman Kodak Company, Rochester, N. Y. New York, Interscience Publishers, Inc., 1949. 479 pages; 57 figures; 21 tables. Price, $9.50.

(*Reviewed by George L. Royer and B. L. West, Calco Chemical Division, American Cyanamid Company, Bound Brook, New Jersey*)

This well-known book on the practical side of dye chemistry first appeared in 1919 and has passed through a number of editions in German and one British translation (1921). This American translation brings into the English language an enlarged up-to-date laboratory manual covering the techniques for the preparation of intermediates and dyes and includes sections on technical details, analytical methods, analysis of commercial dyes, and on lightfastness. Twenty-two types of chemical reactions, such as halogenation, nitration, oxidation, reduction, sulfonation, etc., are well covered by examples in the text and are presented in a special index. Under the heading of intermediates, the preparations of those compounds of the benzene, naphthalene, and anthraquinone series are given in detail. Well-chosen examples of the manufacture of dyes are described for azo, di- and triphenylmethane, oxazine and thiazine, anthraquinone, sulfur, and phthalocyanine dyes.

There are no claims that all the processes are the best possible, but they are all practical and reproducible.

The book should be an excellent laboratory manual, for it gives a good over-all picture of the chemistry of dye manufacture. It should be invaluable not only to the student of dye chemistry alone but also to the student of organic chemistry as well. The textile chemist will obtain from this book a perspective of dye manufacture which he needs to better understand the problems of the synthetic dye chemist and their relation to his own.

The invaluable tables in the back of the book are printed on double-page spreads rather than on the folded sheets as in the Austrian edition, and this will make them stand up better under constant use.

Fibre Science. Edited by J. M. Preston, Manchester, England, The Textile Institute, 1949. 341 pages. Price, $6.00.

(Reviewed by Lee P. Witnauer, Eastern Regional Research Laboratory, Philadelphia, Pennsylvania)

The purpose of this book is to present an up-to-date composite picture of the constitution, structure, and behavior of fibers. The text consists of a series of seventeen Post Advanced Lectures which were given at the College of Technology, Manchester, during the 1947–1948 session. The chapters, although written by different authors, are for the most part inter-related, resulting in a fairly unified volume. The material is presented in a clear, straightforward, and simple manner.

Approximately one-third of the chapters are devoted to the chemistry of various fibers and fiber-forming substances, including cellulose, amylose, chitin, pectic acid, alginic acid, protein fibers, and various synthetic fiber-forming polymers.

Approximately an equal number of chapters are devoted to the methods used in investigating fiber structure. Some of the methods considered are molecular weight and shape determinations, optical properties, and x-ray diffraction studies.

In the remaining chapters such topics as swelling and dispersion, crystalline and amorphous regions, organization of the cell wall in plants in relation to the structure of fibers, and the fine structure of fibers in relation to dyeing and finishing are discussed.

Many of the chapters have extensive bibliographies. There is a subject index but no author index.

The book should be of value to the student and the technologist, and it is also a handy reference work.

ABSTRACTS

SERVICES AVAILABLE

Reprints of the original articles abstracted in TEXTILE RESEARCH JOURNAL *are often available from the publishers. Otherwise, it may be possible to obtain copies of the periodicals. Orders should be sent direct to the publishers.*

Photostat negatives of articles abstracted will be furnished to members of the Institute at a cost of 25 cents per page for pages not exceeding 7 inches in width and 50 cents per page for larger sizes up to 11½ x 14 inches. Photostats of patents are 50 cents per page. The Library's service charge and postage will be added.

Microfilm copies and paper enlargements of microfilm may be obtained from: Microfilms Inc., 313 N. First St., Ann Arbor, Mich.; New York Public Library, New York, N. Y.; Yale University Library, New Haven, Conn.; Harvard University Library, Cambridge, Mass.; and Library of Congress, Washington, D. C. Translations may also be obtained from the above sources.

A list of periodicals, the abbreviations used in reference to articles, and the addresses of publishers of English-language publications is given in the January, 1949, issue, page 46.

CHEMICAL and PHYSICAL RESEARCH

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Carbohydrate-Cuprammonium Complexes

Cuprammonium-glycoside complexes. I. Conducto-metric measurements. R. E. Reeves and J. R. Jung, Jr. *J. Am. Chem. Soc.* **71**, 209–11 (Jan. 1949).

Conductivity measurements are better indications of the formation of cuprammonium complexes than optical rotation data. The conductometric measurements can be used to distinguish between various methyl α-hexosides and between various α- and β-pyranoside pairs. A. R. Macormac

Text. Research J. Oct. 1949

Cuprammonium-glycoside complexes. II. The angle between hydroxyl groups on adjacent carbon atoms. R. E. Reeves. *J. Am. Chem. Soc.* **71**, 212–4 (Jan. 1949).

The position is taken that complex formation between cuprammonium and two hydroxyl groups occurs most rapidly when the hydroxyl groups are located a particular distance apart. Examination of a number of substances having hydroxyl groups on adjacent carbon atoms held more or less rigidly at a number of angles (hence distances) has shown complex formation to occur readily at the true cis-position (0° angle) and at the 60° angle, but not at the 120° or the 180° angle.

Text. Research J. Oct. 1949 Author

Cuprammonium-glycoside complexes. III. The conformation of the D-glucopyranoside ring in solution. R. E. Reeves. *J. Am. Chem. Soc.* **71**, 215–7 (Jan. 1949).

Consideration of the properties of 17 D-glucopyranoside derivatives has led to the conclusion that in this series complex formation between cuprammonium and two hydroxyl groups occurs only with the glycol on the second and third or the third and fourth carbon atoms. Consideration of the behavior of 12 complex-forming glucosides in the light of a previously presented theory reduces from 8 to not more than 3 the number of conformations which need be considered to represent the shape of the pyranoside ring of each glucoside in solution: for 3 of the substances only one ring conformation appears to be possible. It is noted that a single ring formation, the trans "chair form" in which the ring oxygen and the 6-carbon project on the same side of the plane of the 1, 2, 3, 4 carbons, is sufficient to explain the behavior of all complex-forming glucosides in solution. A symbol has been assigned to each of the 8 pyranose stainless ring conformations. Author

Text. Research J. Oct. 1949

Hydration of Cellulose

Mechanism of the hydration of cellulose and its derivatives. G. Champetier and P. Clément. *Bull. soc. chim. Belges* **57**, 236–51 (1948) (in French); cf. *C.A.* **42**, 3562*g* (through *Chem. Abstr.* **43**, 845*h*–846*i* (Jan. 25, 1949)).

H_2O in cellulose (*I*) or its derivatives may be chemically bound or physically absorbed; chemically bound H_2O is determined by using the fact that it does not dissolve a reference compound ($Na_2S_2O_3$). Native *I* has 0.5, regenerated *I* has 1, and mercerized *I* has 0.75–1 molecule of chemically bound H_2O (*II*) per anhydroglucose unit. In cellulose acetate (*III*), *II* attains a maximum of nearly 3 molecules per anhydroglucose unit for monosubstituted *III* and decreases to 1.3 for trisubstituted *III*. *I* takes up 18–30% H_2O from the vapor phase and trisubstituted *III*, approximately 10%; the amounts of *II* for the 2 substances are in the same order of magnitude (5–10%). For cellulose nitrate *II* decreases with increasing degree of substitution and becomes zero for nearly fully substituted material. Curves of *II* against time show that, for *I*, absorption is almost instantaneous; for *III*, most of the H_2O is absorbed in a few minutes (primary hydration) and the rest in 3–100 hrs. (secondary hydration). The results indicate that solvation of the free polar

groups constitutes primary hydration; secondary hydration is an exchange reaction involving hydration of polar groups previously bound by intermolecular or intramolecular association. The wave length and width of the infrared absorption band of the CO group in *III* increase with decreasing degree of substitution; this confirms the above conclusions. The connection between hydration and crystallinity is discussed. 37 references.

Text. Research J. Oct. 1949

Modification of Cellulose

The modification of cellulose by reaction with formaldehyde. I. J. Gruntfest and D. D. Gagliardi. TEXTILE RESEARCH JOURNAL **18**, 643–50 (NOV. 1948).

Experiments relating to the chemistry of the technologically important cellulose-formaldehyde reaction are described. While for many reasons definitive statements about the reaction cannot now be given, certain of its gross features are revealed. As the formalization process is usually carried out, the reaction with cellulose is competitive with the evaporation of the formaldehyde. At low temperatures (to 30°C) no reaction takes place. At higher temperatures (150°C) reaction takes place over a wide range of conditions of acidity. The product formed at high acidity is stable to hydrolysis and is characterized by reduced swelling, increased elastic modulus, and resistance to creep. At lower acidities and under alkaline conditions, the properties of the product are much more like those of the starting material and the formaldehyde is easily removed by washing in neutral aqueous solutions. The combining weight of formaldehyde with cellulose varies, among other things, with the concentration of the formaldehyde applied. The lower the concentration the more nearly the combining weight approaches 12, which corresponds to the formation of simple methylene ethers with the cellulose. At higher concentrations, the combining weight increases toward a value of 30, indicating the formation of polyoxymethylene ether linkages.

Text. Research J. Oct. 1949 Authors

Photolysis of Cellulose

Photolysis of cotton cellulose. I. Production of carbon dioxide on irradiation of cellulose with intense ultraviolet light. V. L. Frampton, L. P. Foley, and H. H. Webber. *Arch. Biochem.* **18**, 345–52 (1948) (through *Chem. Abstr.* **43**, 1563*b* (Feb. 25, 1949)).

Cotton cellulose (*I*) in cupriethylenediamine solution gave a weak absorption in the region 370–400 mμ. Irradiation of *I* in solution did not modify the absorption but caused a decrease in the viscosity. On intense ultraviolet irradiation of dewaxed *I* or *I* regenerated from cupriethylenediamine solution, 0.120–0.170 millimol. of CO_2, but not CO or H, was produced per gram of *I* during 19 hours of irradiation in the absence of O. A post-irradiation production of CO_2 was obtained by passing air over *I* which had been irradiated in a N atmosphere.

Text. Research J. Oct. 1949

Water Sorption and the Structure of Cellulose Fibers

Water sorption and the poly-phase structure of cellulose fibers. J. A. Howsmon. TEXTILE RESEARCH JOURNAL **19**, 152–62 (Mar. 1949).

Many of the methods used to study the fine structure of cellulose are tedious and not suitable for routine use. In the present work, an equilibrium moisture regain method which can be carried out on a large scale with a high degree of accuracy has been developed. The method is illustrated by a wide variety of cellulose materials covering a wide range of moisture sorption capacity. The terms "accessibility" and "crystallinity" are discussed and possible errors arising from assumed equivalence of these terms are pointed out. A preliminary attempt to evaluate both accessibility and crystallinity of cellulose from moisture regain data has been made. This evaluation results in a proposed revision of the scale of reported crystallinities of various types of cellulose. The hydrolysis method for studying cellulose accessibility has been compared with moisture regain and x-ray diffraction methods. It is proposed that recrystallization of cellulose during hydrolysis is a determining factor in this method and, therefore, that published data obtained from hydrolytic studies should be reconsidered. Author

Text. Research J. Oct. 1949

Alpha-Cellulose Determination

Determination of α-cellulose. H. Doering. *Das Papier* **2**, 359–64 (1948) (through *Chem. Abstr.* **43**, 1975*d* (Mar. 10, 1949)).

Inasmuch as Staudinger *et al.* (*C.A.* **37**, 5232[2]) have shown that whereas native cellulose (degree of polymerization (D.P.) 1000) may be insoluble in cold 10% NaOH a regenerated cellulose of the same D.P. may be soluble in this same solution. The author warns against the current neglect of the surface of fibers exposed to alkali when the α-cellulose determination is made. The present standard method used in Germany is therefore open to serious criticism in that dilution with H_2O, prior to filtration of the mercerized cellulose, changes the surface of the fibers. Mechanical shredding of cellulosic material must be eliminated, and after the initial mercerization subsequent changes in exposed surface must be studiously avoided. The following method is proposed: The pulp is defibered carefully, so as not to injure the fibrous structure, and converted into a sheet, which is then air-dried and disintegrated manually; 2.5 g. are treated at 20°C with 30 cc. of 17.5% NaOH with the minimum amount of handling. The suspension is then filtered by suction on a Jena 11G3 crucible and washed successively with 50–100 cc. 10% Na_2SO_4 solution, H_2O, 50–100 cc. *N* H_2SO_4, and H_2O until free from acid. Washing with EtOH is omitted. Results obtained by the author's procedure are invariably higher than those obtained by the usual standard procedure, the difference ranging from 2.1 to 4.2%.

Text. Research J. Oct. 1949

Adhesion of High Polymers to Cellulose

Adhesion of high polymers to cellulose. Influence of structure and tack temperature. A. D. McLaren. *J. Polymer Sci.* **3**, 652–62 (Oct. 1948).

It is shown that the adhesion of high polymers to cellulose is related to the tack temperature and dielectric constant and to the dipole moments of polar groups. Adhesion of a polymer to cellulose, pretreated with chromium complexes of acids, was found to be a function of the polar groups on the polymer and on the cellulose. E. D. Klug

Text. Research J. Oct. 1949

Cellulose Derivatives

The formation of bridged compounds in cellulose fibers with diisocyanates. P. Eckert and E. Herr. *Kunstseide u. Zellwolle* **25**, 204–10 (1947) (through *Chem. Abstr.* **43**, 1563*d* (Feb. 25, 1949)).

See *Chemical Abstracts* for complete abstract.

Text. Research J. Oct. 1949

Solubility of Cellulose Esters

The solution of highly polymeric substances (particulary nitrocellulose) in activated nonsolvents, in the absence of volatile true solvents. K. Thinius. *Farben, Lacke, Anstrichstoffe* **2**, 97–102 (1948) (through *Chem. Abstr.* **42**, 8520*h*–8521*d* (Nov. 10, 1948)).

Clear solutions of nitrocellulose (*I*) are obtained in mixtures of nonsolvents. In alcohol-ether mixtures, the solubility limits vary with the *I* concentration, and the absolute η goes through a minimum which requires more alcohol with increasing *I* concentration; the relative η (η solution/η solvent) shows no minimum, but, with increasing ether concentration, rises suddenly at 60% alcohol, 40% ether. *I* is soluble in mixtures of C_6H_6 with absolute alcohol (*cf.* German Pat. 624,436, *C. A.* **30**, 2780[8]), and in mixtures of 70–60% $C_2H_4Cl_2$, 30–40% PrOH (opaque films), but not in mixtures of $C_2H_4Cl_2$ with 94% EtOH, unless considerable amounts of a good solvent-plasticizer (*e.g.* Bu_3PO_4) are added (*cf.* Fife and Reid, *C. A.* **24**, 3066; Reid and Frazier, *C. A.* **24**, 3660), nor in mixtures of CH_2Cl_2 or CCl_4 with alcohols. Mixtures of ether with higher alcohols are not as effective as solvents of *I* as with EtOH (*cf.* Kraus, *C. A.* **37**, 6453[8]). 10% *I* is soluble in mixtures of 50–30% ether, 40–60% *cyclohexanol*. Another nonsolvent for *I*, *3-chlorodihydropyran* (*II*) (b. 141°C), becomes a solvent in (volume %) mixtures of 25% *II*, 75% of 94% EtOH; 45% *II*, 55% BuOH; 80% *II*, 20% isohexyl alcohol; alcohol-soluble *I* is soluble in 60% *II*, 40% BuOH; *I* lacquers are made from 65% *II*, 15% alcohol, and 20% isodecanol, and from 50% *II*, 12.5% of 94% alcohol, 12.5% BuOH, and 12.5% AmOH, with addition of plasticizers and resins. EtOH or cyclohexanol activates mixtures of *II* with higher alcohols; H_2O does not interfere unless the system separates. *II* mixtures with alcohols up to AmOH can be cut with aromatic hydrocarbons. *Cellulose tripropionate* (*III*) is soluble in the following mixtures: 93–50% toluene, 7–50% MeOH or EtOH (lowest η, 92% toluene; 8% MeOH); 92–40% toluene, 8–60% $MeO(CH_2)_2OH$ (*IV*) (lowest η, 90% toluene, 10% *IV*); PrOH and BuOH are not as effective as activators for toluene; *III* is also soluble in mixtures of 85% CCl_4, 15% MeOH; 90–60% CCl_4, 10–40% *IV*; and 80–60% CCl_4, 20–60% $EtO(CH_2)_2OH$; *III* is not clearly soluble in mixtures of CCl_4 with 94% EtOH. *Secondary cellulose acetate* (*V*) is insoluble in *3-cyanodihydropyran*, but is made soluble by addition of alcohol (at 35°C). Another nonsolvent for *V* is *2-cyano-3-chlorotetrahydropyran* (*VI*). *V* dissolves in mixtures of 20–30% of *VI*, 80–70% MeOH (or EtOH), but not as easily when higher alcohols are used. EtOH also activates mixtures of *VI* with esters of aromatic hydrocarbons which do not dissolve *V*. It is thought that OH compounds add themselves to the *V* molecules and weaken the secondary bonds.

Text. Research J. Oct. 1949

Cellulose Nitrate Reactions

Interaction between cellulose nitrate in solution and inorganic salts. H. Campbell and P. Johnson. *J. Polymer Sci.* **3**, 735–49 (Oct. 1948).

It is shown that gelation of cellulose nitrate in 1%-acetone solution on standing over basic salts is due to COOH or possibly SO_3H groups. In contrast to this gelation, very dilute solutions (less than 0.2% concentration) of cellulose nitrate standing over CaO show a fall in viscosity with time. Ultracentrifuge measurements show that this is not due to degradation; in fact, the higher sedimentation constants indicate that association of part of the nitrocellulose had occurred. No such aggregation occurred in the absence of the CaO. The association process is a first-order reaction which is more rapid at elevated temperatures. Calcium oxide, added to the cellulose nitrate before solution in acetone, did not cause aggregation. E. D. Klug

Text. Research J. Oct. 1949

Cross-linking of Nitrocellulose

Cross-linking of nitrocellulose studied with the ultracentrifuge and consistometer. I. Julliander and B.-S. Blom-Sallin. *J. Polymer Sci.* **3**, 804–11 (Dec. 1948).

Experiments with cross-linking of nitrocellulose in butyl acetate by means of titanium tetrachloride are described. The gels have been examined by means of sedimentation in the ultracentrifuge and measurements with a consistometer. The yield value of the flow curves and the extent of cross-linking were studied as functions of nitrocellulose concentration, amount of cross-linking substance, and time of reaction. Authors

Text. Research J. Oct. 1949

Action of Alkali on Celluronic Acids

Investigation of the properties of cellulose oxidized by nitrogen dioxide. VI. The effect of alkali on the celluronic acids. P. A.

McGee, W. F. Fowler, Jr., C. C. Unruh, and W. O. Kenyon. *J. Am. Chem. Soc.* **70**, 2700–5 (Aug. 1948).

Determinations of carboxyl groups in celluronic acid by alkaline methods are inaccurate because of alkaline degradation. For the same reason, the copper numbers of such products are high. It has been suggested that this alkaline degradation is due to ketone groups, which may rearrange to give an enediol structure. This paper presents a systematic attempt to determine such groups by direct chemical methods. The oxidation of the number-six carbon atom in the anhydroglucose unit of cellulose by nitrogen dioxide is essentially complete at the end of 24 hrs.' reaction time under the experimental conditions used. However, secondary oxidation continues at another position, forming alkali-sensitive linkages. Measurement of ketone groups by the methyl hydroxylamine method of Purvis indicates that celluronic acid, after a 16-hr. oxidation, possesses 1.7% carbonyl by weight, or 1 carbonyl group for each 10 original glucose units. The acidity generated in an alkaline solution at a constant reaction time appears to be directly related to the carbonyl-group content and is an exponential function of the alkali concentration. The ketone groups are believed to enolize in alkali, the enediols split as in simple carbohydrates, the adjacent glucoside links hydrolyze, and an extensive alkaline degradation is thus initiated, which continues along the chain, producing reducing and acidic substances. A. R. Macormac

Text. Research J. Oct. 1949

Diffusion of Dyes

The diffusion of direct dyes into cellulose. II. The interpretation of rate of dyeing measurements. J. Crank. *J. Soc. Dyers and Colourists* **64**, 386–93 (Dec. 1948).

The first part of this paper discusses earlier work on the measurement of the diffusion coefficient and its variation with dye concentrations, and a suggestion is made for improving the accuracy of the results by adopting a different method of mathematical analysis of the measurement. Some recently developed mathematical solutions (results) of the diffusion equation for conditions corresponding to those of the commercial dye bath are shown to lead to calculated rate-of-dyeing curves which are not in agreement with experimental measurements. The subject is discussed under the following headings: (1) diffusion into a plane sheet from an infinite dye bath, and (2) diffusion into yarn of circular cross section from a finite dye bath in which such items as electrical factors, dye-bath concentration, modified surface potential equations for a cylindrical surface, diffusion equation and the new boundary condition, and the relation between effective and total dye-bath concentrations are considered. An interesting result is that, for the cases examined, dyeing from a finite dye bath—*e.g.*, one showing 90% exhaustion—is better represented by the mathematical solution (result) for an infinite dye bath than by the solution (result) actually corresponding to 90% exhaustion. An explanation is advanced in terms of the electrochemical nature of the system, an aspect of the problem which was previously neglected in deriving the mathematical solutions (results). Further experimental data are necessary before the explanation can be adequately tested. C. Amick

Text. Research J. Oct. 1949

Vat Dyes

Stability of vat colors at elevated temperatures. Piedmont Section A.A.T.C.C. *Am. Dyestuff Reptr.* **38**, P213–31 (Mar. 7, 1949).

The dyeing temperature instructions for vat dyes submitted by the dye manufacturer have varied from cold to 180°F, depending upon the type and character of the individual dyestuff. It has been common knowledge to the industry that many types suffer either destruction or change in shade if the temperature is raised or if reduced solutions stand for an abnormal length of time. The recent development of high-temperature dyeing, in which it was desired to use vat colors, has necessitated a search for vat dyes or methods of applying them which would eliminate the tendency to decompose or change shade. Following the selection of suitable analytical methods, potassium hydroxide, potassium carbonate, sodium carbonate, and trisodium phosphate were tested as substitutes for sodium hydroxide in the dye bath, using vat blues of the BCS type in the testing. No advantages were found with these alkalies over sodium hydroxide when this type of color was used. Hydrosulfite, sulfoxylate-hydrosulfite, glucose, commercial molasses and sugars, and sulfide of soda were tested as reducing agents. None of the products tested, or combinations thereof, were superior to hydrosulfite-conc. when used alone. It was observed that dextrine was an aid to the stabilization of reduced vat color solutions. The protective property of dextrine could be determined by an "alkali labile number" (a measure of the dextrine that is readily attacked by alkali). This protection was particularly valuable for the BCS Blues, but was also helpful for many other vats. It is believed that the dextrine buffers the reducing power of caustic and hydrosulfite, preventing continued reduction of the dyestuff itself. However, the action appears to go further than this because a dye bath that has already disintegrated by over-reduction may be partially restored to produce a satisfactory dyeing by the addition of dextrine.

Text. Research J. Oct. 1949 C. A. A.

The absorption of the two vat dyes, Caledon Red and Caledon Jade Green, by cotton. A. Geake. *J. Text. Inst.* **40**, T57–87 (Jan. 1949).

By using Caledon Jade Green, C. I. 1101, and Caledon Red BN, C. I. 1162, two dyes that are sufficiently soluble in suitable organic solvents to allow them to be purified by crystallization and that are sufficiently soluble in pyridine to permit extraction from the dyed fabric and subsequent analysis by spectrophotometric methods, the relation between the composition of the dye

solution and the concentration of the dye in the cotton at equilibrium dyeing conditions was investigated. Although the initial absorption of the dye by the cotton was very rapid, unfortunately the attainment of equilibrium was very slow, the rate being dependent upon the composition of the dye bath as well as upon the temperature and the conditions of agitation. By using dye solutions containing 0.1*M* sodium hydroxide (0.4%) and 0.006 *M* sodium hydrosulfite (0.1%) at 113°F, which are approximately those recommended for commercial dyeing of cotton hanks (in England), it was observed that the concentration of the vat dye in the cotton increased much less rapidly than its concentration in solution. When dyed at the same temperatures (77°F) from vats containing no added salt, Jade Green is absorbed by cotton in much greater amount than Red BN, the concentration of the dye in the equilibrium solution (g./100 ml.) being the same in the two cases. It is well known that Jade Green is much more substantive than Red BN, and this is one of the reasons why the former is a "hot dyeing" and the latter a "cold dyeing" color. When the dye, hydrosulfite, and alkali concentrations of the dye bath were kept constant and increasing amounts of Glauber's salt (anhydrous) were added to the dye bath, an increase in absorption of dye by the cotton was observed, which is presumed to be due to the same cause that produces a similar effect with direct dyes. Increasing additions of pyridine to dye baths having constant composition caused a reduction in the amount of vat dye absorbed by cotton from a solution of its leuco compound. This effect of pyridine is believed to be correlated with its effect in raising the redox potential of the system formed by the solution of the leuco dye in equilibrium with the solid oxidized form. Cotton conditioned for several weeks at 0%, 60%, and 100% R.H. showed different absorption results; that conditioned at 100% R.H. absorbed less dye than that conditioned in drier atmospheres. The rate of dyeing and possibly the equilibrium absorption are shown to be diminished if, before dyeing, the cotton is soaked in water or dilute aqueous solutions and not dried prior to dyeing. The special apparatus and technique designed to give maximum accuracy in the measurements are described, and a number of data on the spectral absorptions of solutions of the purified dyes in various solvents are recorded. Of special interest is the observation that if the dyed yarn was allowed to dry in the air before being dropped into the pyridine, the extraction of the dye from it became much more difficult, and still more so if the drying was completed in a desiccator or oven.

Text. Research J. Oct. 1949 C. Amick

Temperature Dependence of Conductivity and Critical Concentration

The temperature dependence of conductivity and critical concentration of two typical colloidal electrolytes. A. P. Brady and H. Huff. *J. Colloid Sci.* **3**, 511–20 (Dec. 1948).

Conductivity curves for aqueous solutions of lauryl sulfonic acid and potassium laurate were determined at 0°, 25°, 50°, 70°, and 90°C. The critical concentrations, as determined by conductivity, pass through a minimum at about room temperature. This is in fairly good agreement with critical concentrations determined by other methods.

E. D. Klug

Text. Research J. Oct. 1949

D.C. Conduction

D.C. conduction in swollen polymer solutions. I. Electrolysis of the keratin-water system. G. King and J. A. Medley. *J. Colloid Sci.* **4**, 1–7 (Feb. 1949).

It is shown that when a direct current is passed through a keratin film containing at least 15% water, the amount of hydrogen present in the gas evolved is always electrochemically equivalent to the amount of electricity passed. This is assumed to confirm the ionic nature of the conduction process. It is suggested that this is true of all such systems. Authors

Text. Research J. Oct. 1949

D.C. Conductivity of Polar Polymer Adsorbate Systems

The influence of temperature and adsorbed salts on the D.C. conductivity of polar polymer adsorbate systems. G. King and J. A. Medley. *J. Colloid Sci.* **4**, 9–18 (Feb. 1949).

The D.C. conductivity of polar polymer adsorbate systems has been measured for the polymers keratin, gelatin, and nylon over a wide range of adsorbate concentrations, using water and formic acid as adsorbates. The effect of temperature changes and the presence of impregnated salts in the polymer has also been investigated. On the assumption that the conduction process is ionic in nature, it is shown that Bjerrum's relation for ionic dissociation gives an adequate description of the conduction phenomena. Authors

Text. Research J. Oct. 1949

Dynamic Properties

Dynamic properties of filaments, yarns, and cords at sonic frequencies. W. J. Lyons. TEXTILE RESEARCH JOURNAL **19**, 123–35 (Mar. 1949).

A brief description of the stretch-vibrometer developed at the Firestone Research Laboratories is given, and the theory of its operation is outlined. Described are new measurements made on the instrument verifying the previous conclusion that loss of energy to the apparatus is immeasurably small. Values of the dynamic stretch-moduli E, coefficients of internal friction μ, and hysteretic energy losses of 15 samples of natural and synthetic textile materials, Fiberglas, and steel wire are given. Corresponding static values of moduli and energy losses are also given. The latter, it is shown, do not correlate with dynamic values, and hence cannot be regarded as predictive of dynamic behavior. The resonant frequencies at which measurements were made on these samples ranged from 65 to 360 c.p.s. The significance of the various measures which have been employed with the present data to

express hysteretic losses is discussed, and it is shown that the quantity $\mu\omega_0 E$, while not rigidly constant, is confined to a narrow range of values in most samples. Further evidence is submitted generalizing the near-hyperbolic relationship between μ and ω_0. Results of application of the method to the comparisons of various tire-cord rayons are given. Measured on the stretch-vibrometer have been dynamic moduli ranging from 2.1×10^{10} (rubber thread) to 226×10^{10} (steel wire) dynes/cm.^{2}, and internal-friction coefficients from 0.74×10^6 (rubber thread) to 25.7×10^6 (silk thread) poises. Author

Text. Research J. Oct. 1949

Films at Oil-Water Interfaces

Mixed adsorbed films at oil-water interfaces. E. Hutchinson. *J. Colloid Sci.* **3**, 521–9 (Dec. 1948).

Measurements have been made of the interfacial tensions of aqueous solutions of sodium dodecyl sulfate against solutions of octyl alcohol in benzene. By application of the Gibbs adsorption theorem, approximate calculations have been made of the surface excess of alcohol molecules and detergent molecules in the mixed adsorbed interfacial film on the assumption that this film contains no water molecules. The suggestion is made that, for systems in true equilibrium, the effect of oil-soluble impurities in the sodium dodecyl sulfate should be less than in the corresponding experiments in air-water surfaces. The properties of the mixed adsorbed films are intermediate between those of the two pure components. Author

Text. Research J. Oct. 1949

Films at the oil-water interfaces. III. E. Hutchinson. *J. Colloid Sci.* **3**, 531–7 (Dec. 1948).

Measurements have been made of the interfacial tension of aqueous solutions of sodium dodecyl sulfate against benzene, cyclohexane, chlorobenzene, and nitrobenzene by the sessible bubble method. Calculations have been made of the number of molecules of solute adsorbed in the interface on the basis of a monomolecular film, and force-area curves for the adsorbed films of detergent are given. It is shown that, at a nitrobenzene-water interface, the detergent film is more condensed than on a water surface, but at a benzene-water and cyclohexane-water interface the film is more expanded. At a chlorobenzene-water interface the film properties are similar to those of water. The films appear to be imperfect "gaseous"-type films over the range investigated. Author

Text. Research J. Oct. 1949

Phosphonitrilic Chlorides

Photochemistry of phosphonitrilic chlorides. I. A photochemical reaction of low-polymeric phosphonitrilic chloride. B. R. Dishon and Y. Hershberg. *J. Polymer Sci.* **4**, 75–82 (Feb. 1949).

Trimeric and tetrameric phosphonitrilic chlorides, dissolved in hexane, benzene, toluene, or decahydronaphthalene, were irradiated with ultraviolet light. Under these conditions chlorine atoms were replaced by R of the solvent RH.

Text. Research J. Oct. 1949 E. D. Klug

Polymer Adhesion

Adhesion. III. Adhesion of polymer to cellulose and aluminum. A. D. McLaren and C. J. Seiler. *J. Polymer Sci.* **4**, 63–74 (Feb. 1949).

Adhesion of polyvinyl acetate to regenerated cellulose film and to aluminum foil was independent of intrinsic viscosity $[\eta]$, provided $[\eta]$ was above 0.39. When $[\eta]$ is lower than 0.39, cohesive failure of the heat seal occurs. The relationship $[\eta]^{1/\alpha} = K' - B'T$ was derived and shown to hold for polyvinyl acetate (T is tack temperature absolute; a, K, and B are constants). Data on the effect of humidity on adhesion of polyvinyl acetate and polymethyl vinyl ketone are given. The adhesion of vinyl chloride-vinyl acetate-maleic acid copolymer compositions to aluminum attains a maximum at a mole fraction of 0.016 maleic acid in the polymer. Data are given for adhesion of vinyl acetate-methyl vinyl ketone copolymers and vinyl chloride-ethylene copolymers. The effect of temperature on maleic acid copolymers is also considered. E. D. Klug

Text. Research J. Oct. 1949

Elastoviscous Properties of Polymers

Elastoviscous properties of polyisobutylene. I. Relaxation of stress in whole polymer of different molecular weights at elevated temperatures. R. D. Andrews, N. Hoffman-Bang, and A. V. Tobolsky. *J. Polymer Sci.* **3**, 669–92 (Oct. 1948).

The relaxation stress of whole polymer samples of different average molecular weights has been investigated over the range 30–100°C at different elongations. The activation energy for relaxation is independent of the molecular weight. Relaxation rate depends upon molecular weight with sufficient sensitivity so that relaxation measurements may be used to determine the molecular weight. E. D. Klug

Text. Research J. Oct. 1949

Magnetic Rotatory Power of Polymers

Magnetic rotatory power of liquid polymers. R. Lageman. *J. Polymer Sci.* **3**, 663–8 (Oct. 1948).

The Verdet constant of 9 polyethylene glycols, 3 polypropylene glycols, and 9 silicone polymers has been measured at 25°C. It was found that the Verdet constant increases with increase in molecular weight in each of the series, and approaches a constant value. A similar increase in the molecular magnetic rotation was noted. The results are in contrast with those on polystyrene, and the effect of end groups on the measurements is discussed in explanation. Author

Text. Research J. Oct. 1949

Degradation of Polystyrene

Thermal degradation of polystyrene. Part I. H. H. G. Jellinek. *J. Polymer Sci.* **3**, 850–65 (Dec. 1948).

Polystyrene was degraded at 248°–340°C *in vacuo* and distribution

curves of several degraded samples were determined. The data indicate that degradation did not follow the random theory of breaking links. The weak-link theory of degradation is in better agreement with the data. E. D. Klug

Text. Research J. Oct. 1949

Thermal degradation of polystyrene. Part II. H. H. G. Jellinek. *J. Polymer Sci.* **4**, 1–12 (Feb. 1949).

Data are given for the formation of a monomer from polystyrene *in vacuo* at 280° and 307°C. A mechanism based on the assumption that the formation of a monomer is dependent upon the rupture of the chain at a weak point, forming two active chain ends, is proposed. Data on degradation in the presence of oxygen are also given. It is concluded that degradation involves the formation of inhibitors.

Text. Research J. Oct. 1949 E. D. Klug

Thermal degradation of polystyrene and polyethylene. Part III. H. H. G. Jellinek. *J. Polymer Sci.* **4**, 13–36 (Feb. 1949).

The rate of formation of a monomer during the pyrolysis of fractionated and unfractionated polystyrene at 340°–400°C *in vacuo* was determined. Similar data are also given for polyethylene, in the temperature range 281°–363°C, and for polystyrene cross-linked with divinyl benzene, at 364°C. Mechanisms for the degradation are suggested. Polyethylene appears to be more heat-resistant than polystyrene.

Text. Research J. Oct. 1949 E. D. Klug

Cross-Linking of Proteins by Formaldehyde

The reaction of formaldehyde with proteins. V. Cross-linking between amino and primary amide or guanidyl groups. H. Fraenkel-Conrat and H. S. Olcott. *J. Am. Chem. Soc.* **70**, 2673–84 (Aug. 1948).

Simple primary and secondary amines react with formaldehyde and primary amides over the range of pH 3–8 within 24–48 hrs. at room temperature to give condensation products of the general structure R—NR′—CH_2—NH—CO—R″. Representative compounds of this type have been isolated in pure form. The primary reaction is the formation of methylol amines and not methylol amides. *N* = alkyl amides, including peptides (R—NH—CO—R′), do not react in similar systems. Simple amines condense with formaldehyde and guanidines at pH 4–5 but amides and guanidines do not react under the same conditions. Through methylene condensation reactions of these types, formaldehyde permits the introduction of simple amides or guanidines into proteins or macromolecular model substances rich in amino groups, and also permits the introduction of primary amines into proteins or model substances rich in amide groups. Under suitable conditions, small amounts of ammonia or primary amines cause gelation of acid formaldehyde reaction mixtures of gliadin, zein, or polyglutamine, probably by introducing cross-links ($—CH_2—\underset{\displaystyle R}{N}—CH_2—$) between the numerous amide groups in these substances. It appears probable that these cross-linking reactions between amino and primary amide or guanidyl groups contribute greatly to the tanning or hardening action of formaldehyde at room temperature and over a range of pH 2–9 on proteins of average composition. Authors

Text. Research J. Oct. 1949

Formaldehyde Reaction of Rayon

The behavior of various staple rayons toward the formaldehyde reaction. A. Richter. *Melliand Textilber.* **27**, 269–73 (1946); *Chem. Zentr.* **1947**, I, 279–80 (through *Chem. Abstr.* **43**, 1571*e* (Feb. 25, 1949)).

With 30 different types of staple rayon, no relationship was found between the NaOH-solubility and the relative wet strength, degree of polymerization (*DP*), or x-ray orientation. The degree of swelling and x-ray orientation are not inversely proportional. The x-ray orientation is not affected by reaction with HCHO. Rayon with a lower *DP* shows a better HCHO effect. Reducing the swelling with a finishing agent also reduces the NaOH solubility. Relative wet strength and alkali-solubility are then proportional. The behavior of the rayon towards such finishing agents cannot be predicted from an examination of the physical properties.

Text. Research J. Oct. 1949

Swelling of Rayon

The influence of fiber structure on the swelling tendencies of staple rayon. E. Elöd and H. G. Fröhlich. *Melliand Textilber.* **27**, 103–6 (1946); *Chem. Zentr.* **1947**, I, 280; cf. *C.A.* **42**, 7987*f* (through *Chem. Abstr.* **43**, 1571*a* (Feb. 25, 1949)).

The swelling tendencies of cellulose fibers were studied as a function of the fiber dimensions. Tests were made on various types of commercial fibers and on acetylated fiber. The change in the swelling and acetylation rate paralleled the increase in diameter. The swelling tendency decreased with increasing diameter.

Text. Research J. Oct. 1949

Flex Life of Rayon Tire Cord

Flex life of passenger tires—relationship of rayon tire cord dip pickup and cord adhesion. R. T. Murphy, L. M. Baker, and R. Reinhardt. *Ind. Eng. Chem.* **40**, 2292–5 (Dec. 1948).

Treatment of rayon tire cord with adhesive or dip solutions of the reclaimed rubber dispersion GR-S Type III latex, casein type, has been studied to determine the relationship among the quantity of adhesive solids deposited, or dip pickup, single cord adhesion, and tire life under high flex running conditions. Two series of tire tests have shown that tire performance can be improved when lower amounts of dip solids are deposited even though single cord adhesion values are reduced. Authors

Text. Research J. Oct. 1949

Stress-Strain Characteristics of Guaran Triacetate

Stress-strain characteristics of guaran triacetate. C. L. Smart and R. L. Whistler. *J. Polymer Sci.* **4**, 87–96 (Feb. 1949).

Guaran, a straight-chain polyanhydromannose with galactopyranoside side chains, was acetylated to the triacetate with acetic anhydride-pyridine. This product gave a clear, colorless film with a tensile strength of 7.5 kg./mm.^{2} and an elongation of 4% at break. Comparative data are given for the triacetates of cellulose and potato amylose. Stress-strain curves for guaran triacetate plasticized with varying amounts of dibutyl tartarate are also given. E. D. Klug

Text. Research J. Oct. 1949

Viscosity

The viscosity of Newtonian, pseudoplastic, and dilatant liquids. Use in the measurement of the D.P. of high polymers. James G. Krieble and John C. Whitwell. TEXTILE RESEARCH JOURNAL **19**, 253–8 (May 1949).

An equation,

$$\zeta = \frac{\pi R_c^3}{(Z+3)\Gamma}\left(\frac{\Delta PR}{2L}\right)^Z t,$$

for the calculation of the counterpart of viscosity for a pseudoplastic (or dilatant) liquid exists from the relationship existing between $1/t$ and ΔP. Evaluation of ζ and Z defines the liquid property as completely as does η alone for a Newtonian liquid. The counterpart of viscosity-ratio,

$$\frac{\zeta}{\eta_0} = \frac{4}{Z+3}\left(\frac{\Delta PR}{2L}\right)^{Z-1}\left(\frac{t}{t_0}\right),$$

which is independent of the rate of shear and viscometer dimensions, can be used to determine the intrinsic viscosity, $[\eta]$. The general character of the change in Z with the concentration is indicated.

Text. Research J. Oct. 1949 Authors

The viscosity of colloids. W. Philippoff. *Z. Naturforsch.* **3b**, 151–9 (1948); cf. *C.A.* **37**, 3653[5] (through *Chem. Abstr.* **43**, 2487*a* (Apr. 10, 1949)).

To explain the effect of solvent and temperature on the intrinsic viscosity of suspensions, the theories of Staudinger (*C.A.* **28**, 6608[8]), where the suspended particle is regarded as a rigid ellipsoid, and of Kuhn, who regards the particle as a deformable ball, were compared critically. The rigid-ellipsoid theory does not admit of solvent and temperature effects, but they can be deduced from the statistical conception of the deformable ball.

Text. Research J. Oct. 1949

Weathering of Cotton

Deterioration of cotton textiles exposed to the weather. H. Bogaty. *Am. Dyestuff Reptr.* **38**, 253–9 (Mar. 21, 1949).

While much attention has been given to the production and evaluation of weather- and mildew-resistant finishes, the results of exposure tests have often been found to be extremely variable. The data presented in this paper are a part of those obtained in the course of an investigation, initiated at the National Bureau of Standards in 1945 at the request of the National Defense Research Committee, of some aspects of "tropical" deterioration of cotton textiles. The presence of copper naphthenate accelerates deterioration of fabric upon exposure and the same treated fabrics seem to deteriorate "at about the same" rate without regard to place of exposure and climatic variables and irrespective of the amount of copper present. However, copper sulfate-free copper naphthenate (purified in the laboratory) deteriorates fabrics less rapidly than copper naphthenate containing free copper sulfate, but even laboratory-prepared copper naphthenate accelerates loss of strength to some extent. The importance of acidic atmospheric contaminants is discussed. The addition of phenyl salicylate to the copper naphthenate treating bath did not improve the weather resistance of the fabric. Addition of pyrogallol to the copper naphthenate treating bath inhibited degradation but hydroquinone and α-naphthol did not show this effect. The mechanism of the effect of the pyrogallol in the copper naphthenate was not studied. Substitution of copper phenyl naphthenate for copper naphthenate appeared to make a fabric so treated somewhat more resistant to soil burial.

Text. Research J. Oct. 1949 C. A. A.

Action of Papain on Wool

Action of papain on sheep wool. I. A. Schöberl and R. Hamm. *Biochem. Z.* **318**, 331–54 (1948) (through *Chem. Abstr.* **42**, 9184*b* (Nov. 20, 1948)).

Papain activated with HCN can dissociate completely untreated wool into its components at pH 10. It was shown that the HCN reacts with the cystine of the wool, making it liable to the action of the enzyme. About one-half of the wool N goes into solution at pH 10 and the wool suffers a loss in weight. The destruction of the wool is due entirely to the influence of the activated papain and not to the HCN or to the alkali damage. **II.** *Ibid.* 355–72.—When wool is treated at 60°C with papain activated by HCN in the presence of buffers of different pH, a definite optimum is observed at pH 9, when 40% of the wool goes into solution. By raising the papain concentration to 120 mg. (in 30 cc.), as much as 52% is brought into solution, and by repeated changes, even 80% of the wool can be digested under favorable conditions. The remaining fibrillar mass is only slightly attacked by the enzyme. Papain attacks the wool most easily at the beginning of the reaction of HCN with the disulfide bonds of the wool cystine.

Text. Research J. Oct. 1949

Structure and Reactivity of Wool

Structure and reactivity of wool fiber. XVIII. The solubility of chemically treated sheep wool in pancreatin. E. Elöd and H. Zahn. *Melliand Textilber.* **27**, 68–70 (1946); *Chem. Zentr.* **1947**, I, 380; cf. *C.A.* **40**, 6903[8]; **43**, 413*a* (through *Chem. Abstr.* **43**, 2778*h* (Apr. 10, 1949)).

Wool was treated with thioglycollic acid (pH 5.0), NaOH, $NaHSO_3$, HCl, formamide, and H_2O_2 at temperatures between 42° and 122°C; 1.6 to 42% of the wool was dissolved. The x-ray pattern indicated the presence of α-keratin

after treatment with NaOH and thioglycollic acid, and the presence of *d*-keratin after the other treatments. The cystine loss varied from 0 to 95%. The wool digested by pancreatic enzyme after 3–10 days amounted to 10–100%. The samples containing α-keratin were digested to a maximum of 28% although the cystine loss was 67%. The samples containing *d*-keratin were 73–100% digested by the pancreatin. Practical applications might include: the detection of wool damage, the isolation of the especially stable subcutis, and the preparation of digested keratin albumin.
Text. Research J. Oct. 1949

Zein Dispersions

Aqueous zein dispersions. C. W. Ofelt and C. D. Evans. *Ind. Eng. Chem.* **41**, 830–3 (Apr. 1949).

Zein is dispersible in strong alkali metal hydroxides only within the narrow pH range 11.3–12.7. Quaternary ammonium hydroxides are also dispersing agents but are somewhat inferior to the alkali metal hydroxides. Zein is not dispersible in ammonium hydroxide or calcium hydroxide solutions. The amount of alkali required to disperse zein is low; based on the weight of zein, 1.4% to 6.4% of sodium hydroxide is required for a 10% zein dispersion. The dispersibility of zein is attributed to the formation of the alkali salts of the phenolic-hydroxide group of tyrosine. Zein is dispersible also in strong acids (12*N* HCl). The pH dispersion curve, viscosity curves, and stability data are presented for aqueous alkali-zein dispersions. Authors
Text. Research J. Oct. 1949

Formaldehyde Curing of Zein

Formaldehyde curing of zein fibers. Cyril D. Evans and C. Bradford Croston. TEXTILE RESEARCH JOURNAL **19**, 202–11 (Apr. 1949).

Conditions necessary for the rapid formaldehyde curing of zein fibers were investigated and a continuous two-stage curing process was developed. The first stage (precuring) consists of a mild cure to introduce approximately 0.75% formaldehyde into the fiber and produces, after stretching, a fine-diameter fiber of exceptional strength and elasticity. The second stage (postcuring) consists of a strong cure to introduce about 3.0% additional formaldehyde into the stretched fiber to stabilize its length. Formaldehyde is bound under both alkaline and acid conditions, but it is only under acid conditions that any curing occurs. Ammonium salts act as catalysts for the reaction in the pH range 0–4 and the resulting fibers are stable to boiling in mild alkali. When cured under highly acidic conditions (below pH 0), the fibers are stable to both acid and alkaline boiling. Authors
Text. Research J. Oct. 1949

BLEACHING: DYEING: FINISHING

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Fluorescent Bleaching Agents

Fluorescent bleaching agents. A. Landolt. *Textil-Rundschau* **3**, 376–82 (1948) (through *Chem. Abstr.* **43**, 2780*c* (Apr. 10, 1949)).

Bleaching methods are described which use compounds having no color of their own but imparting a brighter appearance to bleached goods by fluorescence and being substantive to fibers. Various substances used (coumarin and stilbene derivatives) are enumerated. Two new "fluorescent bleaching" agents —Uvitex RS (for cellulosic fibers) and Uvitex WS (for wool)—are described and their additional effect, caused by reflection, is demonstrated on samples. Standard bleaching methods can be shortened by applying these agents without damaging the mechanical properties of the fibers.
Text. Research J. Oct. 1949

Sodium Chlorite as a Bleaching Agent

The behavior of sodium chlorite as a bleaching agent. II. E. Elöd and A. Klein. *Melliand Textilber.* **27**, 263–6 (1946); *Chem. Zentr.* **1947, I**, 570; cf. *C.A.* **43**, 1572*e* (through *Chem. Abstr.* **43**, 2780*e* (Apr. 10, 1949)).

By bleaching with $NaClO_2$ under the usual conditions a complete white could not be obtained. High degree of bleaching is only possible below pH 4.5. The disadvantages of this procedure are: the increased tendency to rusting and corrosion of equipment, the tendency of the $NaClO_2$ to spontaneous decomposition, and the tendency of the pH to rise, which necessitates control and adjustment.
Text. Research J. Oct. 1949

Diffusion of Dyes in Cellulose

Diffusion of dyes in cellulose. T. H. Morton. *Textil-Rundschau* **4**, 39–49 (1949) (through *Chem. Abstr.* **43**, 2199*g* (Apr. 25, 1949)).

A review with 35 references.
Text. Research J. Oct. 1949

Dyeing Glass Fibers

Dyeing of glass fibers. F. Gund. *Melliand Textilber.* **27**, 196–8, 232–3, 267–9 (1946); *Chem. Zentr.* **1947, I**, 464 (through *Chem. Abstr.* **43**, 2775*i* (Apr. 10, 1949)).

A review of patents covering the use of binders and surface coatings in the dyeing of glass fibers.
Text. Research J. Oct. 1949

Wool Dyeing

Dyeing wool with chromatable dyes in the presence of chromium salts. E. W. Thommen. *Textil-Rundschau* **3**, 367–76 (1948) (through *Chem. Abstr.* **43**, 2776*h* (Apr. 10, 1949)).

Von Bergen *et al.* (*C.A.* **41**, 7756*d*) proved that nonuniform dyeing of wool tips and roots with chrome dyes in acid baths is principally caused by differences in the constitution of the dyes. In contrast, differences of shades of tips and roots dyed with chrome dyes in neutral Cr salt solutions depend on the state of solution of the dye-Cr salt complex preceding formation of the Cr lake. Wool tips, damaged by photochemical action of light rays, are in a loosened condition; wool roots are not damaged and are more compact. Thus, large dye-Cr salt aggregates can better penetrate tips than roots. Eriochromal mor-

dant TP was developed as a new assistant to neutral chrome dyeings, being capable of dispersing better the colloidal complexes so that the roots are penetrated as well as the tips. Colored and black-white photomicrographs are included.

Text. Research J. Oct. 1949

Vat-Dyeing of Wool

Coloristic studies on the vat-dyeing of wool. G. Nitschke. *Melliand Textilber.* **27**, 96–8, 122–4 (1946); *Chem. Zentr.* **1947, I**, 852 (through *Chem. Abstr.* **43**, 3200*e* (Apr. 25, 1949)).

The merits of the chrome-dyeing and the vat-dyeing processes for the dyeing of wool are discussed. Vat-dyed wool appears to spin better than the chrome-dyed product. The shorter dyeing period, the lower temperature, the saving in $K_2Cr_2O_7$, and the possibility of operation as a continuous process are further advantages of the vat process. Techniques and equipment used in the vat-dyeing process are discussed. The amount of dye remaining in the bath liquor after the first run, and therefore not used, was determined quantitatively. Such dye was used up almost completely by concentrating the bath after the first run and adding fresh wool without the addition of more dye. When indigo was used, a considerable portion of the dye remained in the bath after the first run. This was not prevented even by the addition of $(NH_4)_2SO_4$. Factors affecting fastness and color tone are discussed. No undesirable effects of modern softeners containing oil on vat dyes were observed. The development of a continuous process for the vat-dyeing of loose wool is discussed.

Text. Research J. Oct. 1949

Rayon Slashing

Modern rayon slashers facilitate processing. R. Wilson. *Textile Inds.* **113**, 122–3 (Apr. 1949).

The equipment for the slashing of rayon has been improved to the point that the process is no longer uncertain with respect to quality. Improvements of greatest importance are steam-jacketed size kettles and size vats, stainless steel construction, and automatic controls. Maximum slasher production of 150 yds. per min. is permissible.

A. L. Landau

Text. Research J. Oct. 1949

FIBERS: YARNS: FABRICS: MECHANICAL PROCESSES

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Fibers

Fibers in future fabrics. P. Sillan. *Rayon and Synthetic Texts.* **30**, 41–2 (Mar. 1949).

A review of factors influencing the use of specific fibers in future fabrics. L. A. Fiori

Text. Research J. Oct. 1949

Modern Textile Fibers

The modern textile fibers. L. Rose. *Textile Recorder* **67**, 62–5 (June 1949).

A brief survey of the whole field of man-made fibers, their outstanding properties, and new uses.

Text. Research J. Oct. 1949 L. A. Fiori

Flexibility of Fibers

The flexibility of cotton and rayon staple fibers. O. Heimeran. *Textil-Praxis* **4**, 92–7 (Mar. 1949).

Flexibility is defined as the property which permits fibers to assume a helical form in a yarn. It cannot be measured directly; as a substitute measurement the author and others count the number of rotations of a cylindrical weight suspended on a yarn until the yarn is untwisted sufficiently to break. The mathematical interpretations of this test by authors of earlier papers are discussed, and experimental results for rayon staple and cotton yarns of the same count and for cotton yarns of various counts are given. The torque due to the untwisting of the yarn depends upon the yarn diameter and the kind of fiber.

Text. Research J. Oct. 1949 J. F. Krasny

Processing Synthetic Fibers

Processing continous-filament synthetic fibers. R. A. Hargreaves. *Whitin Rev.* **16**, 22–8 (Feb. 1949); **16**, 13–23 (Mar.–Apr. 1949); **16**, 11–22 (May–June 1949).

A historical review leading up to the development of up-twisters for the twisting of continous-filament synthetic fibers. L. A. Fiori

Text. Research J. Oct. 1949

Structure and Properties of Cellulose Fibers

Certain variations in the structure and properties of natural cellulose fibers. E. E. Berkley. TEXTILE RESEARCH JOURNAL **19**, 363–7 (June 1949).

A discussion of the structure and physical properties of various natural cellulose fibers. X-ray diffraction patterns and schematic diagrams are included.

Text. Research J. Oct. 1949

Medulla and Medullated Wools and Hairs

The medulla and medullated hairs and wools. A. F. Barker. *Textile Manufacturer* **75**, 57–9 (Feb. 1949).

An analysis, illustrated with microphotographs, of certain medullated wool and hair. The wools for Scotch tweeds and the carpet trade are discussed with regard to fiber composition and the effect of medullation. A. L. Landau

Text. Research J. Oct. 1949

Resilience of Fibrous Materials

Volume during and after application of pressure and resilience of fibrous textile materials and their change during processing. H. Mutschler. *Textil-Praxis* **4**, 106–8 (Mar. 1949).

The volumes of several kinds of cotton, wool, and rayon staple in bulk under pressure were compared with the volumes after release of pressure. The same measurements were made on 2 kinds of cotton at various steps in processing—from bale to

yarn. The change in volume after release of pressure is 56–60% for cotton from the bale, 66–68% for card slivers, and 48–50% for yarns.
Text. Research J. Oct. 1949 J. F. Krasny

Yarn Preparation

Yarn preparation discussed by S.T.A. group. Anon. *Textile Bull.* **75**, 43, 44, 46, 48 (May 1949).

A complete recording of the discussion of carding and spinning practices featured at the recent meeting of the Southern Textile Association. A. L. Landau
Text. Research J. Oct. 1949

Yarn Quality

Quality of single yarn in relation to folded yarns. H. Ankers. *Textile Weekly* **43**, 842, 844, 846, 848, 850, 852 (Apr. 15, 1949).

A lengthy review listing defects in single yarns which govern quality of folded yarns. Also considered from a construction viewpoint are the requirements or special features of folded yarns used for different purposes—for example, poplins and Venetians for luster, gabardines for strength and evenness, fancy threads for effects, voiles, crepes, hosiery yarns, lace yarn, and sewing and crochet yarns. Effects of faults of these types of yarn are described.
Text. Research J. Oct. 1949 L. A. Fiori

Fiber Tests Bolster Yarn Strength

Fiber tests can be used to bolster yarn strength. S. Carter. *Textile World* **99**, 118, 119, 245, 246, 248 (Apr. 1949).

The classing, fiber selection, yarn strength, and running quality of the stock can be aided by applying the results of fiber-property research. Such tests can be used to check the ability of the cotton classer, to find the variations, and to determine the effect of the mean fiber length of different bales in each mix when the classified length is the same. It is claimed that the mean length is a better guide than the classified length of the fiber in a mix. The results of tests are reproduced in graphic form.
A. L. Landau
Text. Research J. Oct. 1949

Constant-Speed Yarn Winding

Constant-speed yarn winding. Anon. *Am. Wool and Cotton Reptr.* **22**, 13–14 (June 2, 1949).

In winding, it is claimed, the preferable method is to drive the yarn package on the surface to obtain a constant yarn speed rather than to use a variable yarn speed which results from driving the package from a spindle. In packages of yarn made on winders having a constant-speed surface drive some method of variation must be applied to avoid piling the yarn on the package in ribbons. The merits of open-wind, close-wind, and spool-wind packages are discussed.
A. L. Landau
Text. Research J. Oct. 1949

Fabrics

A fundamental study of some fabric properties. E. Vernon Lewis. *Papers of AATT* **4**, 84–9 (Mar. 1949); *Can. Text. J.* **66**, 42–4 (Mar. 4, 1949).

A report intended to improve present understanding of the aesthetic properties of fabrics which strongly affect their marketability. Fabric properties, such as crease behavior, hand, and drape, are correlated to yarn properties and fabric construction details by means of an assay method which determines from early small samples what contributions the new fiber might make towards fabric appeal. Fundamentals underlying fabric properties and their relation to yarn properties and fabric construction details are developed mathematically.
Text. Research J. Oct. 1949 L. A. Fiori

Bonded Fabrics

The present status of bonded fabrics. R. B. Seymour and G. M. Schroder. *Rayon and Synthetic Texts.* **30**, 49–50 (Feb. 19, 1949); **30**, 43–4 (Mar. 19, 1949).

An extensive review of recent developments of commercial processes for the production of plastic-bonded cellulosic web textiles. 42 references. L. A. Fiori
Text. Research J. Oct. 1949

Nylon Hosiery Sizes

Analysis of nylon hosiery sizes. R. D. Bennet. *Can. Text. J.* **66**, 42, 44 (Apr. 29, 1949).

Methods of evaluating full-fashioned hosiery and circular sizes to assure proper fitting, maximum wear, and consumer satisfaction. L. A. Fiori
Text. Research J. Oct. 1949

Wet Strength of Rayon

The influence of tensioning processes upon the wet strength of rayon fabrics. P. Schmidt and K. Nordmeyer. *Melliand Textilber.* **27**, 126–9 (1946); *Chem. Zentr.* **1947, I**, 279 (through *Chem. Abstr.* **43**, 1571*d* (Feb. 25, 1949)).

Various methods for improving the wet strength of rayon fabrics are discussed. Staple rayon fabric finished with Kaurit MKF or a methylol-melamine resin showed an increase in wet strength from 50 to 70% of the dry strength. Several other commercial resins were tested and suitable plasticizers are suggested.
Text. Research J. Oct. 1949

Blister Rayon Crepe

Blister rayon crepe. Anon. *Am. Wool and Cotton Reptr.* **9**, 9, 10, 15 (Mar. 3, 1949).

Yarns and weaving can be manipulated to produce a great variety of fabric finishes. Special effects may be obtained by weaving together yarns having different degrees and directions of twist.
A. L. Landau
Text. Research J. Oct. 1949

Cloth Faults

Cloth faults and their causes. J. Pollit. *Textile Weekly* **43**, 914, 916, 918, 920, 922, 924, 934 (Apr. 22, 1949).

This report deals with defects detected by visual examination. These defects are classified according to source—that is, process from

opening to doubling, preparation for weaving, weaving, and processes after weaving. Numerous examples of defects and suggestions for remedying them are described briefly. L. A. Fiori

Text. Research J. Oct. 1949

Metallic Sulfide Stains on Wool

Two curious cases of the formation of metallic sulfides. J. Tavernier. *Bull. soc. sci. Bretagne* **22**, 53–6 (1947) (Pub. 1938) (through *Chem. Abstr.* **43**, 924c (Feb. 10, 1949)).

The brown color developed on exposure of a white wool fabric to light and air is attributed to the reaction of S in the wool with Cu and Fe, which probably were introduced from a glycerinated bath used in finishing.

Text. Research J. Oct. 1949

Carding

Fibre arrangement in card slivers. W. E. Morton and R. J. Summers. *J. Text. Inst.* **40**, P106–16 (Feb. 1949).

The experimental technique described in this discussion shows the arrangement of "tracer" fibers in card sliver. Specifically, their disposition as to whether they have leading ends, trailing ends, both ends, or neither end hooked is illustrated by means of an applied method whereby a small portion of the dyed "tracer" fibers is mixed in a lap. To examine these tracers in the resulting card sliver, the sliver is immersed in a liquid of the same or substantially the same refractive index as that of the fibers concerned. Theoretical explanations are given as to the causes of hooked fibers. L. A. Fiori

Text. Research J. Oct. 1949

Sliver formation by carding and alternative methods. W. Hardacre. *J. Text. Inst.* **40**, P132–49 (Feb. 1949).

A detailed account of sliver formation of rayon staple by carding and by means of tow-to-top devices. Speeds, settings, card clothing data, etc., for worsted, flax, and jute cards are tabulated. Ten methods of converting tow-to-top, including the Pacific, Perlock, Greenfield, Phrix, etc., are described—some briefly and some in detail. L. A. Fiori

Text. Research J. Oct. 1949

Jute and Flax Carding

The carding of jute and flax. H. J. Dorman and A. V. Pringle. *J. Text. Inst.* **40**, P117–31 (Feb. 1949).

The problems related to flax, hemp, and jute carding and how they influence the design of the bast fiber card are described. In addition, it is shown how far this design is suited to and what modifications are necessary for the processing of long-staple rayons. L. A. Fiori

Text. Research J. Oct. 1949

Wool Carding

Recent research on the carding of wool. P. P. Townend. *J. Text. Inst.* **40**, P94–105 (Feb. 1949).

This paper describes briefly the more recent experiments on the carding of wool—namely, the mixing action of the card, the effect of cylinder speeds and rate of production on uniformity of slubbing across the card, and the sorting effect of the card. L. A. Fiori

Text. Research J. Oct. 1949

Wool carding. Anon. *Platts Bull.* **6**, 140–3 (Mar. 1949).

Comparison of performance between a standard Semi-Continental set and a shortened Yorkshire set. L. A. Fiori

Text. Research J. Oct. 1949

Woolen Carding Condenser

The woolen carding condenser and its effects on slubbing variation. G. H. Thorndike. *J. Text. Inst.* **40**, P79–93 (Feb. 1949).

An account is given of the manner in which a carded web is divided by the condenser and of the effects of the condenser on the uniformity of woolen slubbing. Comparisons are made between series and endless tape condensers and between intertape and interbobbin differences. Application of graphic results obtained are explained in relation to actual condenser adjustments necessary for the attainment of improved performance. Mention is also made of special techniques for the continuous measurement of slubbing and yarn variations. L. A. Fiori

Text. Research J. Oct. 1949

Waste Carding

Waste carding. Anon. *Platts Bull.* **6**, 128–31 (Mar. 1949).

This discussion provides technical data pertaining to the processing of cotton wastes on both English and Continental carding machines. Typical production data are given for different types of wastes and systems. L. A. Fiori

Text. Research J. Oct. 1949

Continuous Card Stripper

The continous card stripper. Anon. *Saco-Lowell Bull.* **20**, 37–40 (Dec. 1948).

Some "refresher" comments on the installation, maintenance, and supervision of the continous stripper. L. A. Fiori

Text. Research J. Oct. 1949

Roving Defines Card-room Quality

Your roving defines card-room quality. S. Carter. *Textile World* **99**, 133, 135, 196, 198 (Mar. 1949).

Uniform drafting and correct tension are the two most important factors affecting roving quality. Top rolls must be maintained within set limits of diameter. A. L. Landau

Text. Research J. Oct. 1949

Drafting

High drafting and short processing. J. Phethean. *Textile Weekly* **43**, 780, 782, 784, 786, 788, 790, 792, 794 (Apr. 8, 1949).

A comprehensive treatise mainly concerned with short-circuit processing of rovings for ring and mule spinning machines. The economies shown relate only to fly frames, such as slubbers, intermediates, and jack frames. It is generally agreed that by short processing the yarn is much freer from small balls of waste or

neps than ordinary processed yarn. Compared tabularly are drafting and doubling product figures of ordinary and short-circuit processing systems. Comparisons are also made of the staffing requirements of normal machine sequences and short-process practices. L. A. Fiori
Text. Research J. Oct. 1949

French Drawing

The French drawing system. R. S. Audley. *Fibres* **9**, 463–5 (Dec. 1948); **10**, 50–2 (Feb. 1949).

Features of the French drawing system are reviewed briefly.
Text. Research J. Oct. 1949 L. A. Fiori

Drafting Long Fine-Fiber Cottons

Drafting long fine-fiber cottons on super-draft roving frames. J. R. Corley. *Textile Inds.* **113**, 110–13, 223 (Mar. 1949).

Experiments indicate that manufacturer's draft tables do not produce maximum uniformity when processing long, fine-fiber cottons but are more suitable for short-staple fiber. Long-staple cotton was shown to be more sensitive to changes in draft allocation between the front and back drafting zones. The draft guide resulting from this study and the methods employed in testing are reproduced and explained. A. L. Landau
Text. Research J. Oct. 1949

New Drafting System

The Ambler Superdraft System. Anon. *Text. Mercury and Argus* **120**, 767 (May 13, 1949); *Textile Weekly* **43**, 1090 (May 13, 1949).

Known as the Ambler Superdraft System, a new worsted technique for spinning, the invention is said to permit drafts from 20 to 200 when spinning worsteds on orthodox cap, ring, and flyer frames. Only a general description is given, with no technical details. L. A. Fiori
Text. Research J. Oct. 1949

Comber Draw Box

3 over 4 comber draw box (Shaw System). Anon. *Saco-Lowell Bull.* **20**, 29–35 (Dec. 1948).

The Shaw 3-over-4 drafting system, consisting of 3 top rolls working in conjunction with 4 steel bottom rolls, is described in detail. The distinctive feature of this system is the large middle top roll which works in conjunction with the second and third bottom rolls. It is in direct contact with the third bottom roll but a constant positive separation between it and the second bottom roll is maintained by accurately ground discs. In a comparison of this new draw box with the 4-roll "universal" draw box, it was found that the variation ranged from 14% to 18.5% for the latter and 11.9% and 12.5% for the former. Close-up views and sectional drawings are given. This discussion deals specifically with the system's application to the comber draw box. L. A. Fiori
Text. Research J. Oct. 1949

Rewound Filling Versus Ring-Spun Filling

Rewound filling versus ring-spun filling. V. Duxbury. *Textile Manufacturer* **75**, 64–5 (Feb. 1949).

The results of comparative tests showing production figures and costs of a Schweiter winder and a Leesona Number 90 winder used for rewinding filling yarn. Advantages and disadvantages of using rewound filling are given.
A. L. Landau
Text. Research J. Oct. 1949

Lap-Ups on Roll Covering

Don't blame static if cots lap-up. Anon. *Textile World* **99**, 127, 264, 266, 268 (Apr. 1949).

Lapping of fiber on drafting rolls is claimed to be caused by a condition involving an electrokinetic potential at the cot surface. The potential formed is known as the Helmholtz electric double layer, in which layers of positive and negative charges attract and hold each other. In moist cotton mills, it is claimed, a film of moisture is deposited on both the fiber and the cot, with a potential resulting from the electrical attraction of the two films of moisture. The charge is weak and can be neutralized or reduced by the incorporation of electrolytes into the composition of the cot. Methods of testing for the efficiency of cot material are outlined.
A. L. Landau
Text. Research J. Oct. 1949

Loop-Forming Elements

The loop-forming elements. H. Wignall. *Textile Manufacturer* **75**, 62–3 (Feb. 1949).

The first of a series describing the knitting action of a seamless hose machine. The cam layout is illustrated and explained.
A. L. Landau
Text. Research J. Oct. 1949

Spindle Speeds and Yarn Tension

Higher spindle speeds and yarn tension. Anon. *Can. Text. J.* **66**, 46 (Apr. 1, 1949).

Discussed very briefly are the reasons why with higher spindle speeds tension control becomes increasingly important, demanding careful choice of travelers. L. A. Fiori
Text. Research J. Oct. 1949

Cotton Spinning

Cotton spinning technique. W. H. Watson. *Textile Weekly* **43**, 422, 424, 426, 428 (Feb. 25, 1949).

Four important subjects are discussed at some length: (1) the driving of ring spinning machines, (2) condensers in relation to drafting, (3) large packages in mill work, and (4) pneumatic broken-end collectors and other time- and labor-saving ideas. L. A. Fiori
Text. Research J. Oct. 1949

Spinning "Fibro"

Spinning of spun dyed "Fibro." H. Ashton. *Textile Weekly* **43**, 498, 450 (Mar. 4, 1949); **43**, 550, 552, 554 (Mar. 11, 1949).

An outline of the blending technique to be used with "Fibro" in connection with the cotton, worsted, woolen, flax, and jute spinning systems. Stressed are the positions in the sequence of machines where it is advisable to achieve the highest

degree of multiple fiber and color blending. L. A. Fiori

Text. Research J. Oct. 1949

Spinning Staple Nylon

Problems and methods in spinning staple nylon. Anon. *Am. Wool and Cotton Reptr.* **7**, 11–13, 16 (Feb. 17, 1949).

A discussion of the machinery suitable for the processing of nylon staple fiber. Nylon strengthens yarn when blended with other fibers but should be blended only with fibers of the same general characteristics, such as staple length and denier. Temperature and humidity do not affect nylon to the extent that they do other fibers. The main difficulty in processing is the splitting of laps in picking and loading of the licker-in and cylinder at the card. A lower twist multiple should be used at the roving frame.

A. L. Landau

Text. Research J. Oct. 1949

Rayon-Staple Spinning*

Rayon-staple spinning and fibre-blending possibilities. Anon. *Textile Recorder* **67**, 58–61 (June 1949).

A general discussion of (1) effects of staple length and fineness on yarn strengths and upper count limit, (2) fiber blending possibilities, (3) properties of yarns from manufactured fiber blends, and (4) properties of manufactured fiber-natural fiber-blend yarns. Illustrated by 12 charts. L. A. Fiori

Text. Research J. Oct. 1949

Ring Spinning

The traveler movement. W. E. Baltz. *Textil-Praxis* **4**, 162–5 (Apr. 1949).

Small imperfections of the spinning ring cause vibrations of the traveler. Disturbance of the "traveler balance" (TEXTILE RESEARCH JOURNAL **19**, 307 (May 1949)) by this vibration, in resonance with others caused by the traveler rotation and building motion, and its effects on yarn breaks on the spinning frame are discussed. J. F. Krasny

Text. Research J. Oct. 1949

Waste Spinning

Speed frames eliminated in new waste spinning system. Anon. *Text. Mercury and Argus* **120**, 935 (June 17, 1949).

A description is given of a new waste system, called the "Predenser," in which the speed frame has been eliminated and cans are taken directly from the card to the mule.

Text. Research J. Oct. 1949 L. A. Fiori

Proper Spinning Tape Saves Power

Proper tape points way to power savings. R. S. Crowsley. *Textile World* **99**, 126, 127, 214, 216, 218, 220 (Mar. 1949).

The proper selection of spinning tape may reduce power consumption from 7% to 12%. The driving of the spindles requires 33% of the total power needed to operate the standard spinning frame. The width, weave, and thickness of the tape are factors determining tape selection. Charts list the physical properties of various tapes and cylinder-whorl tape ratios.

A. L. Landau

Text. Research J. Oct. 1949

Looms

Loom settings in relation to fabric structure. W. Barker. *Text. Mercury and Argus* **120**, 619–20, 623–4 (Apr. 22, 1949).

Construction features of plain woven structures, twills, drills, and satins are analyzed in relation to the best loom settings necessary for maintaining fabric quality and efficient operating conditions. Such points as shed timings, tensioning of warps, and dobby settings are discussed. A brief review of cloth faults is also given. L. A. Fiori

Text. Research J. Oct. 1949

Weaving

Weavability of modern fibres. J. M. Yerkess. *Textile Weekly* **43**, 864, 866, 868, 870 (Apr. 15, 1949).

Fundamental requirements for a loom for weaving filament synthetic fibers are summarized. Emphasis is placed on the necessity of precision weaving for synthetics since they are characteristically uniform and have no covering properties comparable to those of natural fibers. As a result, weaving irregularties, however slight, are never covered but are actually accentuated in the finished fabric.

Text. Research J. Oct. 1949 L. A. Fiori

Weaving Nylon

Weaving nylons with or without temples. H. E. Wenrich. *Rayon and Synthetic Texts.* **30**, 67–8 (July 1949).

An account of the types of weaves suitable for weaving with and without temples. Instructions for the care of temples and rubber rollers and the setting points to remember when weaving minus temples are also reviewed. L. A. Fiori

Text. Research J. Oct. 1949

Harness and Heddle Faults

Correcting harness and heddle faults. H. E. Wenrich. *Rayon and Synthetic Texts.* **30**, 77–9 (Apr. 1949).

Techniques for replacing missing heddles and for mending damaged and broken ones by the weaver without involving excessive loom stoppage. For cleaning sizing accumulation, it is best to spray a good cleaning solvent into the heddles while the loom is in motion. Other practical suggestions pertaining to heddle and harness maintenance are given. L. A. Fiori

Text. Research J. Oct. 1949

Picker Evener Motions

Picker evener motions. R. Z. Walker. *Textile Bull.* **75**, 45, 46, 48 (Feb. 1949).

A description of the evener motion of the picker. The mechanism regulates the weight of the stock passing over a set of pedals which,

* NOTE: This article was presented by Harold Ashton at one of various meetings in England. Credit is given to him in the discussion. No mention of his name, however, was evident in the heading.

through a series of levers and cross-links, determines the average weight. The feed of stock is controlled by a set of cones to correct the average weight. A. L. Landau

Text. Research J. Oct. 1949

Pickers—The Calender Section

Pickers—the calender section. R. Z. Walker. *Textile Bull.* **75**, 71, 72, 74, 75 (Apr. 1949).

A discussion of the calender section of the modern picker. The use and operation of each subassembly is described. It is recommended that for general mill conditions picker laps should range in weight from 13 to 15 oz. per yd., although there are technicians advocating the use of much heavier laps. The lap meter for testing laps is described.

A. L. Landau

Text. Research J. Oct. 1949

MISCELLANEOUS

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Abrasive Effect of Delustered Rayon

The abrasive effect of delustered rayon on steel needles and card pins. R. Lassé. *Melliand Textilber.* **27**, 81–3 (1946); *Chem. Zentr.* **1947, I**, 477 (through *Chem. Abstr.* **43**, 2779*b* (Apr. 10, 1949)).

Abrasive damage by fibers dulled with TiO_2 is illustrated. The distribution and condition of the TiO_2 particles in the fiber are studied.

Text. Research J. Oct. 1949

Amylase Preparation from Fungi

Preparation of a steeping agent from fungi. R. J. Blaisten. *Rev. asoc. bioquim. argentina* **15**, 47–9 (1948) (through *Chem. Abstr.* **43**, 1571*g* (Feb. 25, 1949)).

Incubation of *Aspergillus niger* and *A. oryzae* in semisubmerged culture on wheat bran at 35°C and pH 4.6 for 3 days gave an amylase preparation 10 times as active as commercial preparations.

Text. Research J. Oct. 1949

Electrostatic Air Cleaning

Electrostatic air cleaning in the textile industry. R. L. Lincoln and T. J. Atkins. *Rayon and Synthetic Texts.* **30**, 94–5 (Mar. 1949).

Discussed in some detail is the electrostatic principle of air cleaning. Electrostatic air cleaners are generally part of the air conditioning or ventilating air system. Basically, this is a device to collect fine dust of low concentration which would normally be found in textile mills. L. A. Fiori

Text. Research J. Oct. 1949

Practical Application of Anti-friction Bearings

Practial application of anti-friction bearings. S. S. Berg. *Textile Bull.* **75**, 51, 52, 54 (Mar. 1949).

A discussion of the improvement in textile machinery through the application of anti-friction bearings. Just previous to 1926, the application of anti-friction bearings to textile machinery commenced, the first points being on the beater shafts and fan shafts of pickers. The cylinders of spinning frames were then equipped with anti-friction bearings, and this was extended to the Pitman roll. It is claimed that anti-friction bearings will pay for themselves, generally within 2 yrs. A. L. Landau

Text. Research J. Oct. 1949

Bleaching Blue Cotton Fiber

A study of the bleaching of blue cotton fiber. R. E. Hudson, Jr., and Howard M. Waddle. TEXTILE RESEARCH JOURNAL **19**, 421–6 (July 1949).

The apparent cause and location of the color in blue cotton has been studied. The color which appeared to be located in the lumen was not particularly resistant to conventional scouring and bleaching agents. The controlling factor in the bleaching of blue cotton appeared to be lack of access to the blue color in the lumen by the treating solution. No ready means of rapid access to the lumen of the whole fiber was found. Diffusion of the blue coloration through the fiber appeared to occur slowly when the fiber was placed in a mildly alkaline bath at elevated temperatures. A bibliography is given. Authors

Text. Research J. Oct. 1949

New Card Clothing

New card clothing cuts need for stripping. G. Zellnik. *Textile World* **99**, 135, 274 (Apr. 1949).

A new type of card clothing for woolen cards is said to reduce stripping time. The foundation is composed of a plastic material with the wire set in the foundation at an angle, eliminating the necessity of bending. The shape of the wire is elongated to provide a streamline effect for greater strength. In one installation after 15 mo., operated 100 hrs. weekly, the clothing had not yet required grinding.

A. L. Landau

Text. Research J. Oct. 1949

Carding History

Carding—evolution and early development. J. G. Martindale. *J. Text. Inst.* **40**, P65–78 (Feb. 1949).

A sketchy review of the first 120 years of the development of woolen and cotton carding machines. 5 references.

Text. Research J. Oct. 1949 L. A. Fiori

Carpet Resilience

Dynamic studies of carpet resilience. J. L. Barach. TEXTILE RESEARCH JOURNAL **19**, 355–62 (June 1949).

The problem of measuring the dynamic properties of a carpet is carried through several different steps which lead to the development of dynamic load measuring equipment designed to evaluate differences of carpet construction.

Text. Research J. Oct. 1949 Author

Analysis of Cellulose

Analysis of cellulose material used in the manufacture of paper. A. Roudier. *Chim. anal.* **30**, 276–80 (1948); cf. *C.A.* **43**, 1185*b*

(through *Chem. Abstr.* **43**, 1565*a* (Feb. 25, 1949)).

The final installment of a paper recounting the analytical results obtained by collaborative work in different laboratories.

Text. Research J. Oct. 1949

Nitration of Cellulose

Rapid method for the preparation of collodion. K. H. Müller. *Süddeut. Apoth.-Ztg.* **88**, 369 (1948) (through *Chem. Abstr.* **43**, 1565*d* (Feb. 25, 1949)).

Explicit directions are given for the nitration of cotton with KNO_3-H_2SO_4. The cellulose nitrate obtained should be dissolved immediately in ether and the EtOH added later. The chemistry of the reactions is discussed.

Text. Research J. Oct. 1949

Cloth Structure

The geometry of cloth structure. J. Pollitt. *J. Text. Inst.* **40**, P11–22 (Jan. 1949).

This report explains the need for cloth geometry and develops important formulas for important structural features of cloth, such as thickness, open spaces, warp and filling crimp, etc. It also demonstrates the uses to which the formulas can be put. L. A. Fiori

Text. Research J. Oct. 1949

Inertia of Rolls

Determination of the inertia of homogeneous rolls or cylinders. R. R. Prechter. TEXTILE RESEARCH JOURNAL **19**, 248–9 (Apr. 1949).

An equation has been developed for determining the inertia, Wk^2, of a roll when the only information given is weight, maximum roll diameter, and core diameter.

Text. Research J. Oct. 1949

Copper Naphthenate

Copper naphthenate as a wood-preserving chemical. A. Minich and M. Goll. *Proc. Am. Wood-Preservers' Assoc.* **1948**, 72–80 (through *Chem. Abstr.* **43**, 2731*e* (Apr. 10, 1949)).

The performance of metallic naphthenates as fungicides is uniform despite variations in the chemical composition of napththenic acids from different sources. Data are given on the solubility in H_2O and in various organic solvents, vapor pressure, and electrical properties of commercially prepared Cu naphthenate. Results of tests on Cu naphthenate as a wood preservative are reviewed. Specifications and methods of analysis are proposed for Cu naphthenate to be used in wood-preserving solutions.

Text. Research J. Oct. 1949

Crease-Resistance and Cotton

Crease-resistance and cotton. G. S. Buck, Jr., and F. A. McCord. TEXTILE RESEARCH JOURNAL **19**, 216–47 (Apr. 1949).

A comprehensive study of the status of crease-resistance as it applies to treatment of textiles. The factors which affect the crease-resistance of textile fabrics are discussed—such as fiber structure and fabric construction. Various crease-resistant finishes are described; also, test methods for evaluating treatments. A brief survey of potential markets for crease-resistant finishes on cottons is included. 165 references.

Text. Research J. Oct. 1949

Cotton Research

Some recent developments in cotton research at the Southern Regional Research Laboratory. Walter M. Scott. TEXTILE RESEARCH JOURNAL **19**, 436–43 (July 1949).

A review.

Text. Research J. Oct. 1949

Retting of Flax

Flax retting with aeration. A process of re-using an industrial waste water. B. A. Southgate. Dept. Sci. Ind. Research (Brit.), Tech. Paper No. **10**, Water Pollution Research, 146 pp. (1948) (through *Chem. Abstr.* **43**, 2438*i* (Mar. 25, 1949)).

Waste water from retting flax by the anaerobic method is very strongly polluting. The polluting character (judged by the amount of 1/80 *N* $KMnO_4$ reduced in 4 hrs. at 26.7°C) of the waste water was reduced by 50% by the addition of $FeCl_3$ or $FeSO_4$. Bleaching powder, $Ca(OH)_2$ (alone or with $FeSO_4$ or $Al_2(SO_4)_3$), or $CaCl_2$ was less effective. The necessity for large-scale waste-water treatment by flax-retting establishments was avoided by re-using the retting liquor and continuously aerating the liquor in the retting tank. Scutched flax of satisfactory quality was produced by this process.

Text. Research J. Oct. 1949

Cottonized bast fiber. V. The chemism of flax decomposition. J. B. A. Stroink, H. J. Bendel, and D. A. Beerens. *Melliand Textilber.* **27**, 139–44 (1946); *Chem. Zentr.* **1947**, I, 475; cf. *C.A.* **40**, 4888^8 (through *Chem. Abstr.* **43**, 3201*h* (Apr. 25, 1949)).

Pectin A binds together the fiber bundles, is soluble in $(NH_4)_2C_2O_4$, and is decomposed and removed during retting. Pectin B is a glucoside bound to the cellulose residues and resists retting. The pectin in the parenchyma is considered to be free, that in the middle layers to be bound to the cellulose by ester linkages, and that in the cell wall to represent galacturonic residues built into glucosides. The oxidation of linen fibers, the influence of alkali on the splitting of the ester bridges and on the degree of polymerization, and the influence of all of these on the staple diagram are discussed. The chemical retting of flax removes first the pectin from the middle layers, then breaks the cross-linkages between the cellulose chains, and finally, by oxidation in alkaline solution, splits the glucose rings. The last process is unfavorable to a uniform staple. In retting with alkali under pressure, the addition of hyposulfite decreases the tendency to form short fibers and yields a cellulose of a higher average polymerization.

Text. Research J. Oct. 1949

Flax Pectin

Flax pectin and flax treatments. H. Rath and A. Agster. *Melliand Textilber.* **27**, 227–31 (1946); *Chem. Zentr.* **1947, I**, 380 (through *Chem. Abstr.* **43**, 2778*d* (Apr. 10, 1949)).

The occurrence, isolation, use, chemical synthesis, properties, esterification, etherification, and reduction of leaching of pectins are discussed. With HCHO the solubility declined sharply up to a certain limit and the pectin increased its degree of polymerization. This increase was smaller for Kaurit WF (a urea-HCHO resin). The flax fiber also showed decreased solubility. $(NH_4)_2C_2O_4$ solution (0.5%) at a temperature below 50°C was suitable for the extraction of high-molecular-weight pectins from flax. The 2 types of pectins (parenchymatous and sclerenchymatous) were similar in synthesis and decomposition. The firm adhesion of the sclerenchymatous pectins is not explained on a chemical basis.

Text. Research J. Oct. 1949

Sources of Cellulose for Rayon

Some promising cellulose-bearing materials (other than cotton) for the manufacture of rayon. M. G. Karnik and D. L. Sen. *J. Sci. Ind. Research* (India) **7**, 351–6 (1948) (through *Chem. Abstr.* **43**, 2768*f* (Apr. 10, 1949)).

Reeds, thorny bamboo (*Bambusa arundinacea*), kamti bamboo, and Manwel bamboo (*Dendrocalamus strictus*) were pulped in 2 stages by using 15% NaOH for 2 hrs. at 20 lb. and 15% NaOH + 5% Na_2S for 6 hrs. at 60 lb.; jute fibers were pulped with NaOH + Na_2S in 2 stages, each for 6 hrs. at 60 lb.; bagasse was pulped with 15% NaOH for 2 hrs. at 20 lb. Pulp yields were 40.3, 40, 37.1, 39.2, 35, 58.9, and 33%, respectively. The chemical compositions of the pulps are given. Viscose was prepared from the pulps from the reeds and bagasse; these take up 85 and 64% of their weight of CS_2 (sulfite pulp takes up 80%). The viscosity of the viscose is 6.1, 28.0, and 30.4, respectively; the viscosity of the viscose from reeds increases more rapidly than that from the other pulps.

Text. Research J. Oct. 1949

Foaming Agent

Analysis and synthesis of peptide-fatty acid condensation products (Lamepons). M. Naudet and P. Desnuelle. *Oléagineux* **3**, 458–63 (1948) (through *Chem. Abstr.* **43**, 3217*e* (Apr. 25, 1949)).

Two commercial products obtained by condensing fatty-acid chlorides with peptides—one a foaming agent for the textile industry and the other a detergent—were analyzed and the results used in preparing similar products. (See *Chem. Abstr.* for complete abstract.)

Text. Research J. Oct. 1949

Sodium Silicates

Industrial applications of the sodium silicates—some recent developments. R. C. Merrill. *Ind. Eng. Chem.* **41**, 337–45 (Feb. 1949).

A review of 116 references. A discussion of the use of sodium silicates as soap builders and textile detergents is included; there are 19 references to their use in textile and allied industries.

A. R. Macormac

Text. Research J. Oct. 1949

Oxidized Surgical Gauze

Oxidation of cellulose. R. L. Kenyon, R. H. Hasek, L. G. Davy, and K. J. Broadbooks. *Ind. Eng. Chem.* **41**, 2–8 (Jan. 1949).

The oxidation of cellulose in the form of rolls of surgical gauze by gaseous nitrogen dioxide, as done on a commercial scale by the Tennessee Eastman Corporation, is discussed in detail. The product is useful as a pharmaceutical raw material because it is soluble at the pH of blood and produces no anaphylactic reaction in the body. The tensile strength of the oxidized gauze is 40% that of the unoxidized material. Other detailed specifications for the product are given.

A. R. Macormac

Text. Research J. Oct. 1949

Second-Hand Kapok

Detection of second-hand kapok. C. M. Jephcott and W. H. H. Bishop. *Anal. Chem.* **21**, 519–23 (Apr. 1949).

100 samples of kapok, consisting of 41 samples of new material and 59 samples of second-hand material, were tested in order to establish a method for detecting the presence of second-hand material. The grade of a sample was judged both by visual inspection to detect signs of general disintegration of the fibers and by the intensity of the fluorescence exhibited under ultraviolet light. Determinations were made of ammonia, urea, sodium sulfate, sodium chloride, pH of the aqueous extract, and oil and fat content. Experiments were performed to determine the specific buoyancy and the percentage loss of buoyancy in 96 hrs. The urea, sodium chloride, oil and fat, and buoyancy tests were found to be of little value and were discarded. The ammonia, sodium sulfate, and pH determinations were found to be practical and standards were adopted: 0.0365% for the ammonia, 0.365% for the sodium sulfate content, and 5.15 for the pH value. The authors consider that a sample of kapok contains second-hand material when the grade is 5 or less and the ammonia content exceeds 0.0365% and either the sodium sulfate content exceeds 0.365% or the pH value is less than 5.15, or both. Authors

Text. Research J. Oct. 1949

Knitting

Whitin Model C-2 tricot knitting machine. Anon. *Whitin Rev.* **16**, 1–6 (Mar.–Apr. 1949).

A general description of the new Whitin Model C-2 tricot knitting machine. L. A. Fiori

Text. Research J. Oct. 1949

Loom Driving

Efficiency in loom driving. H. R. Brammer. *Textile Weekly* **43**,

684, 686, 688, 690 (Mar. 25, 1949).

Described in detail is the new Brammer double-reduction loom clutch drive for looms. It operates by means of a double-reduction drive with a clutch integral acting as an intermediary absorber of the torque factor between the motor and loom drive shaft. This arrangement is a radical departure from conventional loom driving units. Illustrated. L. A. Fiori

Text. Research J. Oct. 1949

Study of Production Looms

Rapid stroboscopic study of production looms. Evans A. LaRoche and Hugh M. Brown. TEXTILE RESEARCH JOURNAL **19**, 288–91 (May 1949).

The authors have developed a phasing arrangement for use with a high-intensity stroboflash lamp for rapidly and accurately checking the timing and for observing the operations of the looms. The test requires no interruption of normal loom operation or alteration of the illumination in the weave room.

Text. Research J. Oct. 1949 Authors

Shuttle Changing Device

New shuttle changing device. Anon. *Text. Mercury and Argus* **120**, 575 (Apr. 15, 1949).

A brief description of a new invention for automatically changing shuttles. L. A. Fiori

Text. Research J. Oct. 1949

Clutsom Shuttleless Machine

The Clutsom shuttleless machine. Anon. *Text. Mercury and Argus* **120**, 467, 469 (Mar. 25, 1949).

High production speeds with considerable saving in labor costs are claimed for this shuttleless loom used for smallware weaving. The principle is described briefly. Illustrated. L. A. Fiori

Text. Research J. Oct. 1949

Nylon in Mixtures

Determination of nylon content in fibre mixtures. R. D. Bennett. *Can. Text. J.* **66**, 58–9, 71 (May 27, 1949).

Described is the latest recommended procedure for analyzing fabrics to determine the nylon content in blends with viscose, acetate, wool, and cotton. L. A. Fiori

Text. Research J. Oct. 1949

Occupational Disease in Nylon Industry

The blood picture of certain workers in the nylon industry. C. Ceresa. *Med. lavoro* **39**, 162–5 (1948) (through *Chem. Abstr.* **43**, 1985g (Mar. 10, 1949)).

Among 27 workers in the nylon industry, especially those handling adiponitrile and hexamethylenediamine, there was found a definite tendency to hyperchromic anemia of the hemolytic type, slight leucopenia, and sometimes lymphomonocytosis.

Text. Research J. Oct. 1949

Modern Lubrication Methods

Modern lubrication methods. Anon. *Textile Inds.* **113**, 87–91 (May 1949).

A detailed discussion of the application of continuous, automatic, and centralized lubricating systems to textile machinery. Such systems have been applied to most of the machinery used in the mill, from the opening room feeder to the loom. A. L. Landau

Text. Research J. Oct. 1949

Centralized Lubrication of Textile Machinery

Centralized lubrication of textile machinery. W. A. Newell and P. M. Thomas. *Textile World* **99**, 115–26 (May 4, 1949).

A complete review of centralized lubrication as used on textile machinery. Actual mill installations of lubricating systems are given describing the advantages as outlined by the mills. Drawings illustrate the lubricating points covered by the centralized lubrication system when applied to various machines. A. L. Landau

Text. Research J. Oct. 1949

Application of Oils to Fibers

Principles of oiling technique. G. Nitschke. *Melliand Textilber.* **28**, 61–2; *Chem. Zentr.* **1947, I**, 858–9; cf. *C.A.* **41**, 3972*h* (through *Chem. Abstr.* **43**, 3203*b* (Apr. 25, 1949)).

The discussion includes a consideration of the various products used for oiling, their application to various types of fibers, and the results of their use. A softener having a high slipping action—*e.g.*, paraffin—should be used for pure wool and that having a good adhesive effect (as a mineral-oil softener) should be used for staple fiber.

Text. Research J. Oct. 1949

Scouring Oil-Lubricated Wool

Scouring mineral oil-lubricated wool. H. R. Hirsbrunner. *Textil-Rundschau* **3**, 342–52, 382–91, 423–9 (1948) (through *Chem. Abstr.* **43**, 2780*b* (Apr. 10, 1949)).

Wool lubricants containing mineral oils are more difficult to remove than those based on vegetable oils. Scouring is influenced by electrical charge, wetting and dispersing properties of the agent, and concentration and temperature of the liquid. Soaps emulsify the best. The colloidal-chemical effects of scouring agents are compared. Mineral oils containing nonsaturated compounds show yellowing in storage and light. Nonscoured or insufficiently scoured wool showed inferior dyeing results after insulation, caused by oil residues. Adsorption of scouring and emulsifying agents also counteracts dye adsorption. Mineral-oil lubricants, based on pure material (*e.g.*, spindle oil), blended with oleic or coconut acids proved best. Tests for determination of oil and soap residues, light discoloration (yellowing), and change in dyeing properties are suggested. 70 references.

Text. Research J. Oct. 1949

Removal of Softeners from Textiles

Determination of the relative ease of removal of softeners from yarns and fabrics. M. Kehren. *Melliand Textilber.* **27**, 159–63 (1946);

Chem. Zentr. **1947**, I, 381–2 (through *Chem. Abstr.* **43**, 2779*e* (Apr. 10, 1949)).

The proper conditions for the removal of certain fiber lubricants were studied. Baths containing soda alone were not effective in removing mineral oil; *synthetic detergents* and emulsifiers such as Igepal W were useful. Raising the temperature to 35°C was also helpful. Temperatures over 45°C damaged woolen fabrics.

Text. Research J. Oct. 1949

Artificial Sponges

Artificial sponges and porous materials from cellulose derivatives. T. Jakobson. *Svensk Papperstidn.* **51**, 447–53 (1948) (through *Chem. Abstr.* **43**, 2427*b* (Mar. 25, 1949)).

A review of literature and patents on pore-forming, coagulating, desulfurizing, washing, drying, impregnating, and after-treatment of foam masses from regenerated cellulose and cellulose acetate. 90 references.

Text. Research J. Oct. 1949

Organic Acids on Stainless Steel

Action of organic acids on stainless steel. C. F. Poe and E. M. Van Vleet. *Ind. Eng. Chem.* **41**, 208–10 (Jan. 1949).

An 18-8 stainless steel was exposed to the action of 0.01*N*, 0.1*N*, and *N* solutions of 12 organic acids for periods up to 10 wks. at 25°C and also in acid baths which were boiled for 30 min. each day. Results are expressed in mg. loss per 100 cm.^{2} surface. The most corrosive acid was *N* oxalic in the solution boiled 30 min. In 10 wks. the loss in weight was 103 mg. Under similar conditions the losses with other acids were: formic, 1.2 mg.; acetic, 1.9 mg.; tartaric, 2.1 mg.; and tannic, 2.0 mg. The corresponding losses at 25°C were: oxalic, 1.3 mg.; formic, 4.6 mg.; acetic, 5.2 mg.; tartaric, 4.6 mg.; and tannic, 0.9 mg. In general, boiling temperatures decreased the corroding action. The corrosive activity is not a direct function of concentration. A. R. Macormac

Text. Research J. Oct. 1949

Temperature Measurements

Temperature measurement of moving textile material. C. W. Bowden, Jr. TEXTILE RESEARCH JOURNAL **19**, 342–5 (June 1949).

The radiation pyrometer has been developed for measuring relatively low temperatures in the range ordinarily encountered in the textile industry. The principle upon which the instrument operates is described.

Text. Research J. Oct. 1949

Products from Wool-Grease

Wool-grease distillation products. I, II. E. S. Lower. *Oil, Colour Trades J.* **115**, 27–8, 30, 32, 84–6 (1949) (through *Chem. Abstr.* **43**, 2449*d* (Mar. 25, 1949)).

A review covering: gas oil, distilled grease, wool-grease olein, wool-grease stearin, and wool-grease pitch. Uses are indicated for the distillation products and some formulas for saddle soaps, floor waxes, etc. Technical journal and patent references are appended.

Text. Research J. Oct. 1949

"Nastrofil" Spinning Frame

The "Nastrofil" spinning frame. Anon. *Textile Weekly* **43**, 558, 560, 562 (Mar. 11, 1949).

This frame converts draw-frame sliver into spun yarn through the use of one machine, resulting in the elimination of all the normal machines from draw frame to ring frame. It embodies these fundamental features: (1) total drafting is obtained by distributing the operation over 5 partially forced draftings or 7 pairs of rollers; (2) drafting is produced in a slow and constant manner, with uniform fiber displacement and control of "floating" fibers; (3) roller pressure is directly proportioned to the quantity of fibers entering between the pairs of drafting rollers. Drafting of over 200 on carded cotton yarns and up to 250 on combed yarns is possible and obtainable in practice. Advantages claimed are increase in production of 10%, a saving in labor of 50%, a lubrication saving of 30%, and a power cost saving of 10%. The system is also known as the "Breda System." L. A. Fiori

Text. Research J. Oct. 1949

Ring Travelers

The spinning traveler. R. S. Audley. *Fibres* **10**, 166–9 (May 1949).

Functions, size, critical speeds, and relevant details of the ring spinning traveler are described briefly. 38 strange patented designs of early ring travelers are illustrated.

Text. Research J. Oct. 1949 L. A. Fiori

New Uptwister

New light-package uptwister. Anon. *Textile Weekly* **43**, 658, 660, 662–3 (Mar. 25, 1949).

This twister, suitable for silk, rayon, and synthetic yarns, takes wound or first-thrown silk or synthetic yarn as the supply package, and in one process of uptwisting produces a cheese or double-ended bobbin suitable for the steamer, dyeing, or other uses. It operates on a wide range of different types of yarns—for hosiery, knitwear, and crepe fabrics—and has the added feature of inserting twist between the extremes of $2\frac{1}{2}$ and 70 turns per in. Detailed descriptions plus close-up views of principle motions are given. L. A. Fiori

Text. Research J. Oct. 1949

Trap Twister

Model K selective-type trap twister. S. B. Hyde. *Whitin Rev.* **16**, 14–21 (Feb. 1949).

Detailed description of a newly designed selective-type twister for the twisting of 2-, 3-, and 4-ply yarns to a large delivery package designed for overend unwinding. A distinguishing feature of this twister is the trap motion which stops yarn delivery functions when the absence of a component yarn in the creel is detected and also when plied yarn between delivery rolls and the

bobbin breaks. Motion is illustrated by close-up views. L. A. Fiori
Text. Research J. Oct. 1949

Worsted Twister

Model R worsted twister. Anon. *Whitin Rev.* **16**, 31–4 (Feb. 1949).

This is a 2-ply sleeve-type trap-motion worsted twister. It features a reciprocating movement of both ring and spindle rails, ensuring a rail traverse of 12 in., depending upon yarn number. This twister can be set to run either on filling or warp wind as desired. Weight of the packages will vary between 24 and 32 oz. It can be creeled from single cone yarn, double cheeses, or spinning bobbins. L. A. Fiori
Text. Research J. Oct. 1949

Drafting System

Another drafting system for roving frames. The Shaw Apron Type FS-2. Anon. *Saco-Lowell Bull.* **20**, 41–50 (Dec. 1948).

Introduced is an all-round Shaw apron drafting unit which operates over a wide range of drafts—up to 40—with equal effectiveness with stock consisting of cotton, a single synthetic fiber, and with blends of any of these fibers. Rolls can be set to process any fiber from $\frac{7}{8}$ in. to $2\frac{1}{2}$ in. Tests reveal a substantial reduction in clearer waste and improvement in roving character. Detailed sectional and close-up views are shown. L. A. Fiori
Text. Research J. Oct. 1949

Yarn Numbering Systems

Universal yarn numbering systems. A. G. Scroggie. TEXTILE RESEARCH JOURNAL **19**, 292–6 (May 1949).

A discussion of the relative merits of the Grex and gK numbering systems.
Text. Research J. Oct. 1949

A universal numbering system for textiles. Anon. *Can. Text. J.* **66**, 52, 54, 56 (May 13, 1949).

The various aspects of a universal numbering system for textiles are considered under 4 headings: (*a*) the need for a universal numbering system, (*b*) the best type of system to employ, (*c*) the units to use, and (*d*) the most suitable dimensions for the preferred units. Also recognized is the need for a concise, non-ambiguous method of designating ply yarns. L. A. Fiori
Text. Research J. Oct. 1949

Larger Yarn Packages

Larger yarn packages. L. D. Sayers. *Textile World* **99**, 108–9 (Apr. 1949).

A comparison of the technical details incorporated in the modernization of the spinning room in a large mill. Spinning bobbins have been increased in length from 10 in. to 12 in. and in diameter from $2\frac{1}{2}$ in. to $2\frac{3}{4}$ in., with a resultant increase in the weight of yarn per bobbin of 54.28%. All technical details are given in the form of comparative charts. A. L. Landau
Text. Research J. Oct. 1949

Periodicals

Chemical periodicals in the dye and textile industries. F. S. Boig and W. J. Fitzpatrick, Jr. TEXTILE RESEARCH JOURNAL **19**, 325–9 (June 1949).

An attempt has been made to determine the more important domestic and foreign journals in the field of dye and textile industries; also, to grade them as to their relative importance and indicate the effects World War II has had on publications in the field. An analysis based on abstracts published in *Chemical Abstracts* was made and the results are tabulated.
Text. Research J. Oct. 1949

Textiles in the Electrical Industry

Textiles in the electrical industry. F. S. Mapes. *Papers of AATT* **4**, 71–4 (Mar. 1949).

Stressed in this report are the advantages and shortcomings of the various textile products—such as cotton, asbestos, glass, rayons, silk, etc.—used for electrical insulation. Particular emphasis is placed on the type of research needed to prevent replacement of textiles by other insulating mediums, such as varnishes, etc. Cotton still seems to be the leading insulating material.
Text. Research J. Oct. 1949 L. A. Fiori

Use-Development Work in Textiles

Scope of use-development work in textiles. H. A. Thomas. *Papers of AATT* **4**, 34–46 (Dec. 1948).

Use-development, defined as the function of finding and developing new and improved uses for established products and for new products, is that integral part of an organization which is concerned with bridging the gap between research and commercial utilization. Comprehensive schematic organizational plans are shown of the relationship of the use-development organization to primary management functions, to scientific research and development, and to sales function. L. A. Fiori
Text. Research J. Oct. 1949

Measuring Wear of Textile Materials

Capacitance method of measuring wear of textile materials. Anon. *Textile Age* **13**, 50, 52, 53 (May 1949).

A non-destructive method for the measurement of abrasive wear of textiles has been developed, depending only upon the change with wear in capacitance of the specimen. Very accurate results have been obtained using only 3 measurements of the fabric to be tested.
A. L. Landau
Text. Research J. Oct. 1949

Consumer Wants

What does the consumer want? J. Labarthe, Jr. *Papers of AATT* **4**, 13–17 (Dec. 1948).

A treatise dealing with consumer complaints, attitudes, and wants. Emphasis is placed on the interpretation and significance of complaints which are presented in tabular form. L. A. Fiori
Text. Research J. Oct. 1949

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